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(71) 出願人 000002185

ソニー株式会社

東京都品川区北品川6丁目7番35号

(72) 発明者 鈴木 祐輔

東京都品川区北品川6丁目7番35号 ソニ

株式会社内

(72) 発明者 渋谷 真志生

東京都品川区北品川6丁目7番35号 ソニ

株式会社内

(74) 代理人 100067736

弁理士 小池 晃 (外2名)

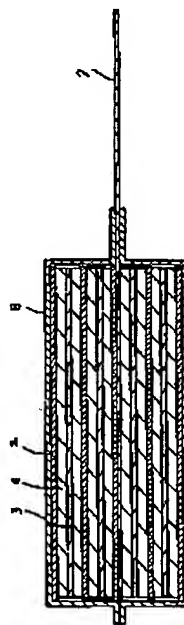
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(54) 【発明の名称】 負極及び非水電解質電池

(57) 【要約】

【課題】 負極活物質として高い放電容量を有する鱗片状黒鉛を用い、高容量かつ高サイクル特性を有し、大電流放電においても高い体積エネルギー密度を示す。

【解決手段】 負極活物質である鱗片状黒鉛と、球状黒鉛、塊状黒鉛、繊維状黒鉛、難黒鉛化炭素又はカーボンブラックのうち少なくとも一種類以上の炭素材料とからなる負極活物質混合体を含有し、当該負極活物質混合体は、上記一種類以上の炭素材料を1重量%以上、50重量%以下の範囲で含有する。



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【特許請求の範囲】

【請求項1】 負極活物質である鱗片状黒鉛と、球状黒鉛、塊状黒鉛、繊維状黒鉛、黒鉛化炭素又はカーボンブラックのうち少なくとも一種類以上の炭素材料とからなる負極活物質混合体を含有し、

当該負極活物質混合体は、上記一種類以上の炭素材料を1重量%以上、50重量%以下の範囲で含有することを特徴とする負極。

【請求項2】 リチウムをドーブ・脱ドーブ可能な正極活物質を有する正極と、

リチウムをドーブ・脱ドーブ可能な負極活物質を有する負極と、

正極と負極との間に介在される非水電解質とを備え、上記負極は、負極活物質である鱗片状黒鉛と、球状黒鉛、塊状黒鉛、繊維状黒鉛、黒鉛化炭素又はカーボンブラックのうち少なくとも一種類以上の炭素材料とからなる負極活物質混合体を含有し、

当該負極活物質混合体は、上記一種類以上の炭素材料を1重量%以上、50重量%以下の範囲で含有することを特徴とする非水電解質電池。

【請求項3】 上記非水電解質は、電解質と膨潤溶媒とを含有する非水電解液がマトリクスポリマによってゲル状とされてなるゲル状電解質であることを特徴とする請求項2記載の非水電解質電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、非水電解質電池に関する。

【0002】

【従来の技術】近年、携帯電話、ノートブック型パソコンなどをはじめとする電子機器のコードレス化、ポータブル化が進み、薄型、小型、軽量の携帯電子機器が次々と開発されている。また、機器の多様化によって電力使用量が増加し、それら電子機器のエネルギー源である電池、特に二次電池の高容量化に対する需要が高まっている。

【0003】従来から使用されてきた二次電池としては鉛蓄電池、ニッケルカドミウム電池があり、新たな二次電池としてはニッケル水素電池やリチウムイオン電池が実用化されている。しかしながら、これらの二次電池は電解質として液状電解質を使用しているため、電池からの液漏れの問題があった。そこで、このような問題を解決すべく開発されたのが、電解液によって膨潤した高分子ゲルを電解質として使用した固体電解質リチウムイオン二次電池である。この固体電解質リチウムイオン二次電池の開発により、電池からの液漏れの心配がなくなり、小型、軽量、薄型であり高いエネルギー密度を有する二次電池の開発が可能となった。

【0004】上記の固体電解質リチウムイオン二次電池の構成について説明すると、アルミニウム薄板からなる

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正極集電体上に、例えば LiCoO_2 と黒鉛とを含有する正極活物質層が形成されて正極を構成している。また、銅薄板からなる負極集電体の上にはカーボン、コークス、グラファイトなどを含有する負極活物質層が形成されて負極を構成している。

【0005】正極と負極との間にはポリプロピレン、ポリエチレンなどからなり、細孔を有する薄膜であるセパレータが組み込まれている。そして、これら電極、セパレータの間には、ポリアクリロニトリル(PAN)、ポリエチレンオキシド(PEO)、ポリフッ化ビニリデン(PVDF)のような高分子をリチウム塩を含む電解液によって膨潤させた、ゲル状電解質が充填されたサンドイッチ構造をとっている。また、サンドイッチ構造になったこれら素電池(ユニットセル)は、封入用容器としてアルミニウム箔のような金属薄膜と、ナイロン、ポリエチレン、ポリプロピレン、ポリエチレンテレフタレート等のプラスチックフィルムで構成された封入材でパッケージングされる。

【0006】さらに負極活物質についてみると、黒鉛自体のリチウム吸蔵、放出能力とともに、電池という限られた体積の中でいかに多量の黒鉛を詰め込みうるかという充填性がある。これは黒鉛に限らず、粉末であればその形状に大きく左右されるものである。黒鉛の粉末の形状を考えた場合、球状、塊状、鱗片状、繊維状等が挙げられる。

【0007】通常、固体電解質負極は、集電体である金属薄膜の両面、又は片面に黒鉛と結着剤との混合物を塗布し、これを適宜圧延して形成されるが、上記各形状の黒鉛のうち鱗片状黒鉛は、圧延によって粒子が同一方向に配向するという特徴により、緊密性が大きく、充填性も大となり、これらの点から黒鉛由来の負極材料としては、鱗片状黒鉛が最も優れた材料であるといえる。

【0008】

【発明が解決しようとする課題】しかしながら、鱗片状の黒鉛を負極活物質として用いる場合、解決しなければならない問題がある。第一に、鱗片状黒鉛は配向性が大きいために、圧延により充填性が上がるが、逆に充填性が上がりすぎて電極内の空孔部分が制限され、電池の電極を形成したとき電極内部に電解質が浸透しないため電極表面部分でしか電池反応が行われず、電極の反応利用率の低下、あるいは高負荷放電に適さないという課題が生じる(特開平8-287952号公報)。

【0009】特にゲル状電解質を用いた電池においては、上記のような課題を解決するため、ゲル状電解質自身が電極中に浸透することが必要とされる。ゲル状電解質は従来の液系電解質と比較して非常に粘度が高いことから、電極塗膜中への浸透は起こりにくい。従って電解液の浸透のみを考慮すれば解決される液系電解質の場合と比較して、電極中における適当な空孔を確保することはより一層重要となる。

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【0010】第二に、負極活物質として鱗片状黒鉛のみを用いて電極を形成した場合、集電体と活物質との間の結着性が、球状黒鉛などのそれと比較して低いため、活物質が充放電を繰り返す際の膨張収縮などによって電極からの活物質の剥離が生じサイクル特性が低下する。これを防ぐために結着剤成分を増加させることは、結果として電極の充放電容量を低下させることになるという問題が生じる。

【0011】本発明はこのような従来の実情に鑑みて提案されたものであり、負極活物質として高い放電容量を有する鱗片状黒鉛を用い、高容量かつ高サイクル特性を有し、大電流放電においても高い体積エネルギー密度を示す負極及びそれを用いた非水電解質電池を提供することを目的とする。

【0012】

【課題を解決するための手段】本発明の負極は、負極活物質である鱗片状黒鉛と、球状黒鉛、塊状黒鉛、繊維状黒鉛、難黒鉛化炭素又はカーボンブラックのうち少なくとも一種類以上の炭素材料とからなる負極活物質混合体を含有し、当該負極活物質混合体は、上記一種類以上の炭素材料を1重量%以上、50重量%以下の範囲で含有することを特徴とする。

【0013】上述したような本発明に係る負極では、負極活物質である鱗片状黒鉛に、球状黒鉛、塊状黒鉛、繊維状黒鉛、難黒鉛化炭素又はカーボンブラックの、他の形状の黒鉛が混合されているので、結着剤成分を増加させることなく負極活物質層と負極集電体との結着性を高めるとともに、負極活物質の利用効率が向上する。

【0014】また、本発明の非水電解質電池は、リチウムをドーブ・脱ドーブ可能な正極活物質を有する正極と、リチウムをドーブ・脱ドーブ可能な負極活物質を有する負極と、正極と負極との間に介在される非水電解質とを備える。そして、本発明の非水電解質電池は、上記負極が、負極活物質である鱗片状黒鉛と、球状黒鉛、塊状黒鉛、繊維状黒鉛、難黒鉛化炭素又はカーボンブラックのうち少なくとも一種類以上の炭素材料とからなる負極活物質混合体を含有し、当該負極活物質混合体は、上記一種類以上の炭素材料を1重量%以上、50重量%以下の範囲で含有することを特徴とする。

【0015】上述したような本発明に係る非水電解質電池では、負極活物質である鱗片状黒鉛に、球状黒鉛、塊状黒鉛、繊維状黒鉛、難黒鉛化炭素又はカーボンブラックの、他の形状の黒鉛が混合されているので、結着剤成分を増加させなくても、負極活物質層と負極集電体との結着性を高めるとともに、負極活物質の利用効率が向上する。そして、そのような負極を用いた本発明に係る非水電解質電池は、高容量かつ高負荷、高サイクル特性を有するものとなる。

【0016】

【発明の実施の形態】以下、本発明の実施の形態につい

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て説明する。

【0017】本実施の形態に係るゲル状電解質電池1の一端成例を図1及び図2に示す。このゲル状電解質電池1は、帯状の正極2と、正極2と対向して配された帯状の負極3と、正極2及び負極3上に形成されたゲル状電解質層4とを備える。

【0018】そして、このゲル状電解質電池1は、ゲル状電解質層4が形成された正極2とゲル状電解質層4が形成された負極3とが積層されるとともに長手方向に巻回された、図3に示す電極巻回体5が、絶縁材料からなる外装フィルム6により覆われて密閉されている。そして、正極2には正極端子7が、負極3には負極端子8がそれぞれ接続されており、これらの正極端子7と負極端子8とは、外装フィルム6の周縁部である封口部に挟み込まれている。

【0019】正極2は、正極活物質を含有する正極活物質層が、正極集電体の両面上に形成されている。この正極集電体としては、例えばアルミニウム箔等の金属箔が用いられる。

【0020】正極活物質としては、目的とする電池の種類に応じて、金属酸化物、金属硫化物、又は特定の高分子を使用することができる。

【0021】例えば、リチウムの溶解・析出を利用したリチウム電池とする場合、 TiS_2 、 MoS_2 、 NbSe_2 、 V_2O_5 等のリチウムを含まない金属硫化物あるいは酸化物、さらにはポリアセチレン、ポリピロール等の高分子を使用することもできる。

【0022】リチウムイオンのドーブ・脱ドーブを利用したリチウムイオン電池とする場合には、 Li_xMO_y （式中Mは一種以上の遷移金属を表し、xは電池の充放電状態によって異なり、通常0.05以上、1.10以下である。）を主体とするリチウム複合酸化物等を使用することができる。このリチウム複合酸化物を構成する遷移金属Mとしては、Co、Ni、Mn等が好ましい。このようなリチウム複合酸化物の具体例としては LiCoO_2 、 LiNiO_2 、 $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ （式中、 $0 < y < 1$ である。）、 LiMn_2O_4 、 LiMPO_4 （式中、MはFe等、一種以上の遷移金属を表す）等を挙げることができる。これらのリチウム複合酸化物は、一種類を単独で用いてもよいし、複数種を混合して用いてもよい。

【0023】リチウム複合酸化物は、高電圧を発生でき、エネルギー密度的に優れた正極活物質となる。正極活物質には、これらの正極活物質の複数種を併せて使用してもよい。また、以上のような正極活物質を使用して正極活物質層を形成するときには、公知の導電剤や結着剤等を添加することができる。

【0024】また、負極3は、負極活物質と結着剤とを含有する負極活物質層が、負極集電体の両面上に形成されている。この負極集電体としては、例えば銅箔等の金

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屑箔が用いられる。負極活物質にはリチウムをドーブ、脱ドーブできる炭素材料が用いられる。

【0025】リチウムをドープ、脱ドープできる炭素材料としては、具体的には後述するが、鱗片状黒鉛が用いられる。そして、このゲル状電解質電池では、負極活物質である鱗片状黒鉛と、当該鱗片状黒鉛に加えて、球状黒鉛、塊状黒鉛、繊維状黒鉛、難黒鉛化炭素又はカーボンブラックのうち少なくとも一種類以上の炭素材料とを含有する。また、以上のような負極活物質を使用して負極活物質層を形成するときには、公知の結着剤等を添加することができる。

【0026】ところで、負極活性物質層に用いられる結着剤は、負極活性物質のようにリチウム吸蔵放出能力を持たない。そのため、結着剤量の増加は負極活性物質の充填量低下につながり、充放電容量を低下させてしまう。

【0027】本発明者らは、鋭意検討を行った結果、負極活性物質である鱗片状黒鉛に他の形状の黒鉛を少なくとも1種類混合することで、結着剤成分を増加させることなく、負極活性物質層と負極集電体との結着性を高めるとともに負極活性物質の利用効率を向上することができ、それにより高容量かつ高負荷、高サイクル特性を示す非水電解質電池を実現できることを見出した。

【0028】すなわち、本実施の形態に係るゲル状電解質電池1では、負極活物質である鱗片状黒鉛と、当該鱗片状黒鉛に加えて、球状黒鉛、塊状黒鉛、繊維状黒鉛、針黒鉛、炭素又はカーボンブラックのうち少なくとも一種以上の炭素材料とを含有する。

【0029】鱗片状黒鉛に加えて混合される、球状黒鉛、塊状黒鉛、微粒状黒鉛、難黒鉛化炭素又はカーボンブラックは、鱗片状黒鉛と同様に、それ自身がリチウム吸蔵放出能力を有する。これらの炭素材料の少なくとも一種類以上を混合することで、結着剤成分を増加させることなく、負極活性物質と負極集電体との結着性を高めることができた。さらに、炭素材料の少なくとも一種類以上を混合することで、着当な適当な空隙を形成することになり、負極活性物質である鱗片状黒鉛へのリチウムイオンのドーブ・脱ドーブが行われやすい構造となる。これにより、鱗片状黒鉛の利用率を向上させて、高い充放電容量を保持したまま、高負荷特性、高サイクル特性を示す電池を得ることができるとする。

【0030】 無機活物質である鱗片状黒鉛と混合される球状黒鉛、塊状黒鉛、繊維状黒鉛、難黒鉛化炭素又はカーボンブラックの量は、鱗片状黒鉛と混合される上記一種類以上の炭素材料及とらなる無機活物質混合体の全体に対して1重量部以上、50重量部以下の範囲であることが好ましい。

【0031】球状黒鉛、塊状黒鉛、楕状黒鉛又は鱗黒鉛化炭素又はカーボンブラックの混合量が、負極活物質混合体全体に対して1重量部未満だと、負極集電体と負極活物質層との密着性を高める効果が不十分であり、長

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期充電サイクルに伴い負極集電体と負極活物質層との界面で割離が生じ、サイクル特性が低下してしまう。

【0032】また、球状黒鉛、塊状黒鉛、繊維状黒鉛又は黒鉛鉛化炭素又はカーボンブラックの混合量が、負極活性物質混合体全体に対して50重量部を超えると、ほとんどは負極活性物質である鱗片状黒鉛の割合が減少してしまい、容量低下を招いてしまう。なお、球状黒鉛、塊状黒鉛、繊維状黒鉛又は黒鉛鉛化炭素又はカーボンブラックの混合量が、負極活性物質混合体全体に対して20重量部を超えると、負極集電体と負極活性物質層との結着性はそれ以上は大きく向上しない。また、十分に大きい値となる。

【0033】さらに、鱗片状黒鉛に球状黒鉛又はカーボンブラックを混合する場合、これら球状黒鉛又はカーボンブラックの単位重量当たりの充放電容量は、鱗片状黒鉛の充放電容量と比較して低いことから、鱗片状黒鉛の割合減少に伴い、容量増加の効果が半減してしまう。さらに、鱗片状黒鉛の減少は、電極塗布膜厚の増加を招くことから、これは、電池の体積エネルギー密度の減少を招く。また、鱗片状黒鉛に難黒鉛化炭素を混合する場合、容量低下は生じないものの、難黒鉛化炭素特有のなだらかな放電曲線を示すことから、携帯電話等の用途に用いるには適当ではない。

【0034】従って、鱗片状黒鉛に対する、球状黒鉛、塊状黒鉛、繊維状黒鉛、黒鉛鉛化炭素又はカーボンブラックの混合量を、負極活性物質混合体全体に対して1重量部以上、50重量部以下の範囲とすることで、高い充放電容量を保持したまま、負極活性物質層と負極集電体との結着性を高めるとともに、負極活性物質の利用効率を向上させて高負荷特性、高サイクル特性を実現することができる。また、球状黒鉛、塊状黒鉛、繊維状黒鉛、黒鉛鉛化炭素又はカーボンブラックの混合量のより好ましい混合量は、負極活性物質混合体全体に対して5重量部以上、30重量部以下の範囲である。

【0035】ゲル状電解質層4は、電解質塩と、マトリクスポリマと、可塑剤としての膨潤溶媒とを含有する。

【0036】電解質塩としては、 LiPF_6 、 LiBF_4 、 $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ 、 $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ 、又は LiCF_3SO_3 等のリチウム化合物を単独又は混合して使用することができる。その中でも、イオン伝導性等の観点から、 LiPF_6 を使用することが好ましい。

【0037】また、マトリクスポリマとは、ポリマ単体もしくはこれを用いたゲル状溶媒が、室温で1 mS/cm以上のイオン伝導度を示すものであれば、特に化学的構造は限定されない。このマトリクスポリマとしては、ビニリデンフルオリド、アクリロニトリル、エチレンオキシド、プロピレンオキシド、又はメタクリルニトリルのうちの少なくとも1つが、繰返し単位として含まれる化合物が使用される。具体的には、ポリビニリ

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デンフルオライド、ポリアクリロニトリル、ポリエチレンオキシド、ポリプロピレンオキシド、又はポリメタクリルニトリルなどが挙げられる。

【0038】また膨潤溶媒としては、エチレンカーボネート、プロピレンカーボネート、ジメチルカーボネート、エチルメチルカーボネート、ジエチルカーボネート、γ-ブチロラクトン、エチルプロピルカーボネート、ジプロピルカーボネート、ブチルプロピルカーボネート、ジブチルカーボネート、1, 2-ジメトキシエタン、1, 2-ジエトキシエタン等の非水溶媒を単独又は混合して用いることができる。

【0039】電極巻回体5は、このような正極2及び負極3のそれぞれの片面に上述したゲル状電解質層4を塗布した後、ゲル状電解質層4を塗布した面を台わせることによって形成される。

【0040】外装フィルム6は、上記極極巻回体5を収容する。外装フィルム6は、例えば、外装保護層と、アルミニウム層と、熱溶着層（ラミネート最内層）とからなるヒートシールタイプのシート状ラミネートフィルムにより形成されている。

【0041】ここで、熱溶着層及び外部保護層の材質としては、プラスチックフィルムなどを挙げることができる。熱溶着層を形成するプラスチックフィルムには、ポリエチレン、ポリプロピレン、ナイロン（商品名）などが用いられるが、熱可塑性のプラスチック材料であればその原料を問わない。

【0042】上述したような本実施の形態に係るゲル状電解質電池1は、負極活物質である鱗片状黒鉛に他の形状の黒鉛を少なくとも1種類混合することで、結着剤成分を増加させることなく、負極活物質層と負極集電体との結着性を高めるとともに負極活物質の利用効率を向上させることができ、それにより高容量かつ高負荷、高サイクル特性を示すものとなる。

【0043】そして、上述したような本実施の形態に係るゲル状電解質電池1は、つぎのようにして製造される。

【0044】まず、正極2としては、正極活物質と結着剤とを含有する正極合剤を、正極集電体となる例えばアルミニウム箔等の金属箔上に均一に塗布、乾燥することにより正極活物質層が形成されて正極シートが作製される。上記正極合剤の結着剤としては、公知の結着剤を用いることができるほか、上記正極合剤に公知の添加剤等を添加することができる。

【0045】次に、正極シートを帯状に切り出す。そして、正極活物質層の非形成部分にリード線を溶接して正極端子7とする。正極端子7に使用される材料の例としては、アルミニウム、チタン、或いはこれらの合金などが挙げられる。このようにして帯状の正極2が得られる。

【0046】また、負極3は、負極活物質と結着剤とを

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含有する負極合剤を、負極架橋体となる例えば銅箔等の金属箔上に均一に塗布、乾燥することにより負極活物質層が形成されて負極シートが作製される。ここで、この負極合剤には、負極活物質である鱗片状黒鉛と、当該鱗片状黒鉛に加えて、球状黒鉛、塊状黒鉛、繊維状黒鉛、離黒鉛化炭素又はカーボンブラックのうち少なくとも一種以上の炭素材料とからなる負極活物質混合体が用いられる。また、上記負極合剤の結着剤としては、公知の結着剤を用いることができるほか、上記負極合剤に公知の添加剤等を添加することができる。

【0047】次に、負極シートを帯状に切り出す。そして、負極集電体の負極活物質層の非形成部分にリード線を溶接して負極端子8とする。負極端子8に使用される材料の例としては、銅、ニッケル、又はこれらの合金などが挙げられる。このようにして帯状の負極3が得られる。

【0048】次に、正極活性物質層及び負極活性物質層上にゲル状電解質層4を形成する。ゲル状電解質層4を形成するには、まず、非水溶媒に電解質塩を溶解させて非水電解液を作製する。そして、この非水電解液にマトリクスポリマを添加し、よく攪拌してマトリクスポリマを溶解させてゲル状の電解質溶液を得る。

【0049】次に、この電解質溶液を正極活性物質層及び負極活性物質上に所定量塗布する。続いて、室温にて冷却することによりマトリクスポリマがゲル化して、正極活性物質層及び負極活性物質上にゲル状電解質層4が形成される。

【0050】そして、以上のようにして作製された帯状の正極2と負極3とを、ゲル状電解質層4を介して張り合わせてプレスし、電極積層体とする。さらに、この電極積層体を長手方向に巻回して電極巻回体5とする。

【0051】最後に、この電極巻回体5を、絶縁材料からなる外装フィルム6で挟み、そして、外装フィルム6の外周縁部を封口し、正極端子7と負極端子8とを外装フィルム6の封口部に挟み込むとともに電極巻回体5を外装フィルム6中に密閉する。さらに、外装フィルム6によってパックされた状態で、電極巻回体5に対して熱処理を施す。以上のようにしてゲル状電解質電池1が完成する。

【００５２】なお、上述した実施の形態では、帯状の正極２と帯状の負極３とを積層し、さらに長手方向に巻回して電極巻回体６とした場合を例に挙げて説明したが、本発明はこれに限定されるものではなく、矩形状の正極２と矩形状の負極３とを積層して電極積層体とした場合や、電極積層体を交互に折り畳んだ場合にも適用可能である。

【００５３】また、上述した実施の形態では、非水電解質電池として、ゲル状電解質を用いたゲル状電解質電池１を例に挙げて説明したが、本発明はこれに限定されるものではなく、非水電解液を用いた非水電解液電池や、

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質層上に均一に塗布し、含浸させ、常温で8時間放置し、ジメチルカーボネートを気化、除去してゲル状電解質層を得た。

【0064】そして、以上のようにして作製された正極と負極とを、ゲル状電解質層が形成された側を対向させて張り合わせ、長手方向に巻回することで、5 cm×4 cm×0.4 cmの高極巻回体を得た。

【0065】この電極巻回体を、ポリプロピレン／アルミニウム／ナイロンの3層構造からなるラミネートフィルムにて密閉することによりゲル状電解質電池を得た。なお、このとき、正極端子と負極端子とを外装フィルムの封口部に挟み込んだ。

【0066】実施例2)負極活物質混合体を構成する鱗片状黒鉛と球状黒鉛との比を95:5の割合としたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状ニッケル電池を作製した。

【0067】〈実施例3〉負極活物質混合体を構成する鱗片状黒鉛と球状黒鉛との比を80:20の割合としたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0068】〈実施例4〉負極活物質混合体を構成する鱗片状黒鉛と球状黒鉛との比を70：30の割合としたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0069】〈実施例5〉負極活物質混合体を構成する鱗片状黒鉛と球状黒鉛との比を60：40の割合としたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0070】〈実施例6〉負極活物質混合体を構成する鱗片状黒鉛と球状黒鉛との比を50:50の割合としたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0071】〈実施例7〉球状黒鉛に代えて塊状黒鉛を用い、負極活性物質混合体を構成する鱗片状黒鉛と塊状黒鉛との比を80:20の割合としたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0072】（実施例8）球状黒鉛に代えて塊状黒鉛を用い、負極活性物質混合体を構成する鱗片状黒鉛と塊状黒鉛との比を60：40の割合としたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0073】《実施例9》球状黒鉛に代えて繊維状黒鉛を用い、負極活物質混合体を構成する鱗片状黒鉛と繊維状黒鉛との比を80：20の割合としたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0074】（実施例10）球状黒鉛に代えて鱗黒鉛化炭素を用い、負極活性物質混合体を構成する鱗片状黒鉛と鱗黒鉛化炭素との比を80：20の割合としたこと以外

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は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0075】〈実施例11〉球状黒鉛に代えてカーボンブラックを用い、負極活性物質混合体を構成する鱗片状黒鉛とカーボンブラックとの比を80：20の割合としたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状水分解電池を作製した。

【0076】〈実施例12〉鱗片状黒鉛と球状黒鉛とカーボンブラックとが80：15：5の比で混合されてなる負極活物質混合体を用いたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0077】（実施例13）鱗片状黒鉛と球状黒鉛と繊維状黒鉛とが80：15：5の比で混合されてなる負極活物質混合体を用いたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0078】〈比較例1〉負極活物質として鱗片状黒鉛のみを用いたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0079】〈比較例2〉負極活物質混合体を構成する鱗片状黒鉛と球状黒鉛との比を9.5：0.5の割合としたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0080】〈比較例3〉負極活物質混合体を構成する鱗片状黒鉛と球状黒鉛との比を30：70の割合としたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0081】（比較例4）負極活物質として球状黒鉛のみを用いたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0082】比較例5) 球状黒鉛に代えて塊状黒鉛を用い、負極活性物質混合体を構成する鱗片状黒鉛と塊状黒鉛との比を40:60の割合としたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状高解質電池を作製した。

【0083】〈比較例6〉球状黒鉛に代えて繊維状黒鉛を用い、負極活物質混合体を構成する鱗片状黒鉛と繊維状黒鉛との比を40:60の割合としたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0084】〈比較例7〉球状黒鉛に代えて難黒鉛化炭素を用い、負極物質混合体を構成する鱗片状黒鉛と難黒鉛化炭素との比を40:60の割合としたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0085】(比較例8) 球状黒鉛に代えてカーボンブラックを用い、負極活物質混合体を構成する鱗片状黒鉛とカーボンブラックとの比を40:60の割合としたこ

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と以外は、実施例 1 と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0086】〈比較例9〉鱗片状黒鉛と球状黒鉛とカーボンブラックとが40:40:20の比で混合されてなる負極活性物質混合体を用いたこと以外は、実施例1と同様にして負極を作製し、この負極を用いてゲル状電解質電池を作製した。

【0087】そして、以上のようにして作製されたゲル状電解質電池について、負極集電体-負極活性物質層間の剥離強度、負極活性物質の放電容量を測定し、さらに、作製したゲル状電解質電池についての負荷特性及びサイクル特性の特性評価試験を行った。

【0088】負極集電体-負極活物質層間の剥離強度は、いわゆるT字剥離試験により測定した。

【0089】1字剥離試験は、図4に示すように、幅30mm、長さ200mmの負極3の、負極活性物質3a表面に粘着テープ10を貼り、さらにこの負極集電体3b側をステンレス板11上に貼り付け、図4中A部分を固定した。この一部を剥がし、その剥がした端をステンレス板11に対して水平方向、すなわち図4中天印B方向に引っ張ることによって10cm剥がした。この時に要した力の平均値を剥離強度とした。

【0090】負極活性物質の放電容量については、同じ負極活性物質混合体を用いて図5に示すようなコイン型電池20を作製し、このコイン型電池20を用いて評価した。

【0091】コイン型電池20の作成方法としては、まず上述の方法と同様にして得られる負極合剤を集電体となるニッケルメッシュ（ニッケル繊維径20 μ m）上に塗布し、乾燥して負極活物質層を形成した。そして、負極活物質層が形成されたニッケルメッシュを、直径15.5mmの円板状に打ち抜くことによりペレット状の負極21とした。

【0092】また、リチウム金属箔を負極と略同形に打ち抜くことにより正極22とした。

【0093】また、エチレンカーボネートと、プロピレンカーボネートとの等容量混合溶媒中に、 LiPF_6 を 1mol/l の濃度で溶解させることにより非水電解液を調製した。

【0094】以上のようにして得られた負極21を負極缶23に収容し、正極22を正極缶24に収容し、正極22と負極21との間に、ポリプロピレン製多孔質膜からなるセパレータ25を配した。正極缶24及び負極缶23内に非水電解液を注入し、正極缶24と負極缶23とを絶縁ガasket 26を介してかしめて固定することにより、直径が20mm、厚さが2.5mmのコイン型電池20を作製した。

【0095】そして、得られたコイン型電池20について、理論容量の10時間率充電を定電圧定電流充電で下限0Vまで行い、次に10時間率定電流放電を終止電圧

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1. 5V間で行った。この時の放電容量を負極活物質の放電容量とした。

【0096】負荷特性としては、ゲル状電解質電池について、まず理論容量の1/3時間率放電(3C)を行い、つぎのように評価した。まず、各電池に対して、23℃、定電流定電圧充電を4.2Vまで10時間行い、次に3Cの定電流放電を終止電圧3.2V間で行い放電容量を決定した。そして、これから求められる平均電圧から各時間率放電での出力を1/5Cに対する100分率として算出した。また、このときの放電容量に対する電池の体積エネルギー密度を算出した。

【0097】サイクル特性としては、各電池に対して、

23℃で定電流定電圧充電を上限4.2Vまで行い、次に、理論容量の2時間率放電(1/2C)の定電流放電を終止電圧3.2V間で行った。これを1サイクルとして500サイクル繰り返した。そして、これから求められる平均電圧から時間率放電での出力をサイクル初期(第1サイクル目)の1/5Cに対する100分率として算出した。

【0098】実施例1～実施例13、比較例1～比較例9の電池についての各電池特性評価結果を表1に示す。

【0099】

【表1】

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実施例	添加炭素材料の種類	炭素材料添加量 (wt%)	負極厚み (mm)	負極剥離強度 (g/mm)	放電容量 (mAh/g)	負極特性 (%)	3C放電の10分間電圧 (V/L)	サイクル特性 (%)
比較例1	球状黒鉛	0	1.00	10.4	358	70	3.21	68
比較例2	球状黒鉛	0.5	1.03	10.6	358	70	3.30	78
比較例3	球状黒鉛	2.0	1.06	20.3	358	82	3.60	63
比較例4	球状黒鉛	3.0	1.08	24.8	350	81	3.64	83
比較例5	球状黒鉛	4.0	1.15	23.6	348	83	3.50	84
比較例6	球状黒鉛	5.0	1.21	23.3	343	84	3.26	87
比較例7	球状黒鉛	2.0	1.06	18.2	353	80	3.38	81
比較例8	球状黒鉛	4.0	1.06	14.6	342	78	3.42	80
比較例9	球状黒鉛	2.0	1.06	14.6	370	72	3.32	65
比較例10	球状黒鉛	2.0	1.06	11.2	373	76	3.01	70
比較例11	カーボンブラック	2.0	1.06	11.2	348	74	3.22	50
比較例12	球状黒鉛+カーボンブラック	1.5+5	1.06	19.4	345	78	3.27	77
比較例13	球状黒鉛+繊維状黒鉛	1.5+5	1.07	21.8	355	78	3.42	79
比較例14	球状黒鉛	0	1.00	3.3	360	34	1.88	33
比較例15	球状黒鉛	0.5	1.00	3.2	360	36	1.83	32
比較例16	球状黒鉛	7.0	1.25	24.3	336	88	3.02	88
比較例17	球状黒鉛	1.00	1.40	24.3	336	88	3.02	88
比較例18	球状黒鉛	6.0	1.23	16.8	344	81	3.12	81
比較例19	繊維状黒鉛	8.0	1.24	17.8	350	78	3.14	79
比較例20	繊維状黒鉛	6.0	1.26	16.3	378	74	3.01	70
比較例21	カーボンブラック	8.0	1.30	10.7	337	74	2.64	48
比較例22	球状黒鉛+カーボンブラック	4.0+2.0	1.31	22.1	336	76	2.71	76

【0100】まず、負極集電体-負極活物質層間の剥離強度についてみると、炭素材料を添加しなかった比較例1及び添加量が0.5重量%の比較例2では、剥離強度が極端に低く、負極活物質層が負極集電体から剥離しやすいことがわかる。添加した炭素材料の割合の増加に伴って剥離強度も増加するが、炭素材料の割合が2.0重量%程度になると飽和し、それ以降は、炭素材料の添

加割合が増加しても、剥離強度の向上はほとんど見られない。

【0101】また、負極集電体-負極活物質層間の剥離強度が大きくなるほど、電池のサイクル特性も良好な値が得られていることがわかる。

【0102】一方、炭素材料の添加割合が増えるに従って、負極活物質の割合が低下することになり、放電容量

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は低下してしまう。また、負荷特性についても、炭素材料の添加割合が5重量%程度までは向上効果が顕著にみられるが、それ以上になると添加炭素材料の特性が強くなり、負荷特性の向上効果はそれほど見られなくなる。

【0103】また、電池の単位面積あたりの放電容量を等しくしようとした場合、炭素材料の添加量が増加するに従って、負極の厚みが厚くなることから、このことは、炭素材料を添加することによって電池の体積エネルギー密度を低下させることを意味する。3C放電時の体積エネルギー密度については、炭素材料の添加量が5重量%以上、30重量%以下のときに、良好な値が得られていることがわかる。

【0104】以上の結果から、負極活物質である鱗片状黒鉛に添加する炭素材料の添加量を、1重量%以上、50重量%の範囲としたときに、好ましい結果が得られていることがわかった。その中でも、炭素材料の添加量を5重量%以上、30重量%以下の範囲としたときに特に好ましい結果が得られていることがわかった。

【0105】

【発明の効果】本発明では、負極活物質である鱗片状黒*

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*鉛に、球状黒鉛、塊状黒鉛、繊維状黒鉛、難黒鉛化炭素又はカーボンブラックのうち少なくとも一種類以上の炭素材を混合することで、結着剤成分を増加させることなく、負極活物質層と負極集電体との結着性を高めるとともに、負極活物質の利用効率を向上させて、高容量かつ高負荷、高サイクル特性を有する非水電解質電池を実現することができる。

【図面の簡単な説明】

【図1】本実施の形態に係るゲル状電解質電池の一構成例を示す斜視図である。

【図2】図1中、X-X'線における断面図である。

【図3】正極及び負極が電極巻回体とされた状態を示す斜視図である。

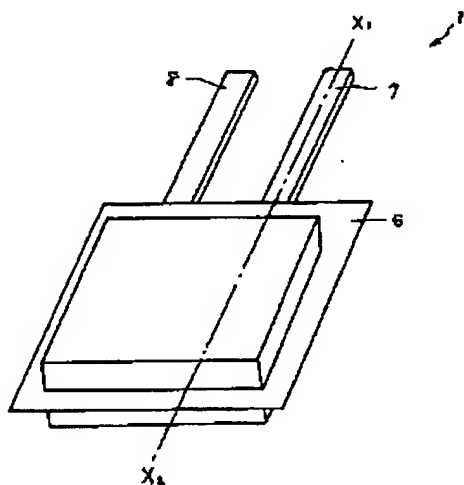
【図4】実施例における剥離強度試験の方法を模式的に示す断面図である。

【図5】負極放電容量の評価で用いたコイン型電池の構成例を示す断面図である。

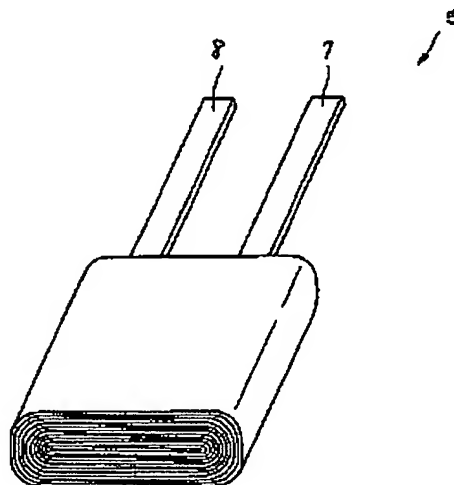
【符号の説明】

1 ゲル状電解質電池、2 正極、3 負極、4 ゲル状電解質層、5 電極巻回体、6 外装フィルム、7 正極端子、8 負極端子

【図1】



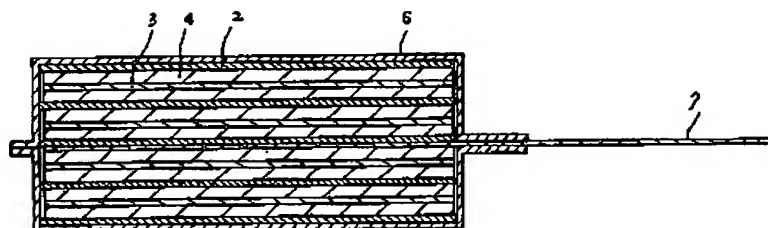
【図3】



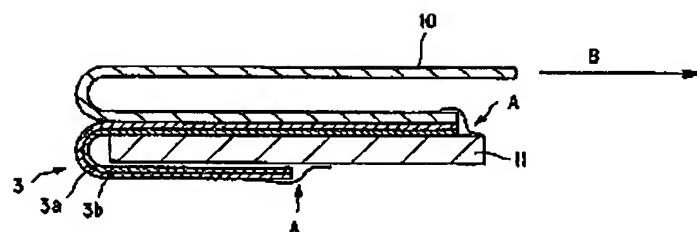
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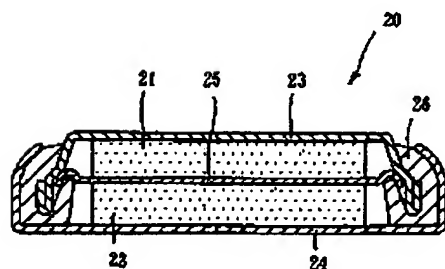
【図2】



【図4】



【図5】



フロントページの続き

(72)発明者 原 富太郎
東京都品川区北品川6丁目7番35号 ソニ
ー株式会社内

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Title: **JP2002008655A2: NEGATIVE ELECTRODE AND NON-AQUEOUS ELECTROLYTE CELL**

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Inventor: SUZUKI YUSUKE;
SHIBUYA MASHIO;
HARA TOMITARO;

Assignee: SONY CORP
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Priority Number: 2000-06-20 JP2000000185070

Abstract:

PROBLEM TO BE SOLVED: To provide a non-aqueous electrolyte cell having high capacity and high cycle characteristics, and showing high volume energy density also in a large current discharge by using a scale-like graphite having high discharge capacity as a negative electrode active material.

SOLUTION: The negative electrode consists of a scale-like graphite which is a negative electrode active material, and a mixture of the negative electrode active materials containing at least one or more kinds of carbon material among a spherical graphite, a massive graphite, fiber-like graphite, and a graphitization-resistant carbon or a carbon black. And, the mixture of the negative electrode active materials contains the above one or more kinds of carbon materials in a range of not less than 1 weight %, and not more than 50 weight %.

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Other Abstract Info: CHEMABS 136(05)072323G CHEMABS 136(05)072323G DERABS C2002-333538 DERABS C2002-333538



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to a nonaqueous electrolyte cell.

[0002]

[Description of the Prior Art] In recent years, cordless-izing including electronic equipment, such as a cellular phone and a book type personal computer, and portable-ization progress, and a thin shape and small and lightweight pocket electronic equipment are developed one after another. Moreover, the amount of the power used increases by diversification of a device, and the need over high-capacity-izing of the cell which is the energy source of these electronic equipment, especially a rechargeable battery is increasing.

[0003] There are a lead accumulator and a nickel-cadmium battery as a rechargeable battery used from the former, and the nickel hydride battery and the lithium ion battery are put in practical use as a new rechargeable battery. However, since these rechargeable batteries were using the liquefied electrolyte as an electrolyte, they had the problem of the liquid spill from a cell. Then, the solid electrolyte rechargeable lithium-ion battery which used as an electrolyte the macromolecule gel swollen by the electrolytic solution was developed that such a problem should be solved. By development of this solid electrolyte rechargeable lithium-ion battery, worries about the liquid spill from a cell disappeared, and development of the rechargeable battery which are small, lightweight, and a thin shape and has a high energy density was attained.

[0004] If the composition of the above-mentioned solid electrolyte rechargeable lithium-ion battery is explained, the positive-active-material layer containing LiCoO_2 and a graphite is formed on the positive-electrode charge collector which consists of aluminum sheet metal, and the positive electrode is constituted. Moreover, on the negative-electrode charge collector which consists of copper sheet metal, the negative-electrode active material layer containing carbon, corks, graphite, etc. is formed, and the negative electrode is constituted.

[0005] It consists of polypropylene, polyethylene, etc. between a positive electrode and a negative electrode, and the separator which is the thin film which has pore is incorporated. And between these electrodes and separator, the sandwich structure with which the gel electrolyte made to swell a polyacrylonitrile (PAN), a polyethylene oxide (PEO), and a macromolecule like a polyvinylidene fluoride (PVDF) by the electrolytic solution containing lithium salt was filled up is taken. Moreover, the packaging of these unit cells (unit cell) that became a sandwich structure is carried out to a metal thin film like an aluminum foil as a container for enclosure by the enclosure material which consisted of plastic film, such as nylon, polyethylene, polypropylene, and a polyethylene terephthalate.

[0006] When it furthermore sees about a negative-electrode active material, there is restoration nature how a lot of graphites can be stuffed in limited volume called a cell with the lithium occlusion of the graphite itself and discharge capacity. If this is not only a graphite but powder, it will be greatly influenced by the configuration. When the configuration of the powder of a graphite is considered, the shape of a globular shape, mass, and a scale and fibrous ** are mentioned.

mentioned negative electrode becomes from at least one or more kinds of carbon materials among scale-like graphite [whose nonaqueous electrolyte cell of this invention is a negative-electrode active material], nodular-graphite and massive graphite, fibrous graphite, and difficulty graphitized carbon, or carbon black -- a mixture -- containing -- the negative-electrode active material concerned -- a mixture is characterized by containing the one or more above-mentioned kinds of carbon materials in 1 % of the weight or more and 50% of the weight or less of the range

[0015] By the nonaqueous electrolyte cell concerning this invention which was mentioned above, while raising the binding property of a negative-electrode active material layer and a negative-electrode charge collector even if it does not make a binder component increase since the graphite of other configurations of nodular-graphite, massive graphite, fibrous graphite, and difficulty graphitized carbon or carbon black is mixed by the scale-like graphite which is a negative-electrode active material, the use efficiency of a negative-electrode active material improves. And the nonaqueous electrolyte cell concerning this invention using such a negative electrode has high capacity and a heavy load, and a high cycle property.

[0016]

[Embodiments of the Invention] Hereafter, the gestalt of operation of this invention is explained.

[0017] The example of 1 composition of the gel electrolyte cell 1 concerning the gestalt of this operation is shown in drawing 1 and drawing 2 . This gel electrolyte cell 1 is equipped with the gel electrolyte layer 4 formed on the band-like positive electrode 2, the band-like negative electrode 3 which countered with the positive electrode 2 and was allotted, and a positive electrode 2 and a negative electrode 3.

[0018] And this gel electrolyte cell 1 is covered with the sheathing film 6 with which the electrode winding object 5 which was wound around the longitudinal direction, and which is shown in drawing 3 consists of an insulating material, and is sealed while the laminating of the positive electrode 2 in which the gel electrolyte layer 4 was formed, and the negative electrode 3 in which the gel electrolyte layer 4 was formed is carried out. And the positive-electrode terminal 7 is connected to a positive electrode 2, the negative-electrode terminal 8 is connected to the negative electrode 3, respectively, and these positive-electrode terminals 7 and negative-electrode terminals 8 are put between the obturation section which is the periphery section of the sheathing film 6.

[0019] The positive-active-material layer in which a positive electrode 2 contains a positive active material is formed on both sides of a positive-electrode charge collector. As this positive-electrode charge collector, metallic foils, such as an aluminum foil, are used, for example.

[0020] As a positive active material, a metallic oxide, metallic sulfide, or a specific macromolecule can be used according to the kind of cell made into the purpose.

[0021] For example, when considering as the lithium cell using the dissolution and the deposit of a lithium, macromolecules, such as metallic sulfide which does not contain the lithium of TiS_2 , MoS_2 , NbSe_2 , and V_2O_5 grade or an oxide and also a polyacetylene, and polypyrrole, can also be used.

[0022] When considering as the lithium ion battery using the dope and the ** dope of a lithium ion, the lithium multiple oxide which makes a subject Li_xMO_2 (the inside M of a formula expresses the transition metals more than a kind, and x changes with charge-and-discharge states of a cell, and it is usually 0.05 [or more] and 1.10 or less.) can be used. As transition metals M which constitute this lithium multiple oxide, Co, nickel, Mn, etc. are desirable. as the example of such a lithium multiple oxide -- LiCoO_2 , LiNiO_2 , and $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$ (it is $0 < y < 1$ among a formula.), and LiMn_2O_4 , LiMPO_4 (M expresses the transition metals more than kinds, such as Fe, among a formula), etc. can be mentioned One kind may be independently used for these lithium multiple oxides, and two or more sorts may be mixed and used for them.

[0023] A lithium multiple oxide can generate the high voltage and serves as a positive active material which was excellent in energy density. You may use two or more sorts of these positive active materials for a positive active material collectively. Moreover, when forming a positive-active-material layer using the above positive active materials, a well-known electric conduction agent, a well-known binder, etc. can be added.

[0024] Moreover, the negative-electrode active material layer in which a negative electrode 3 contains a negative-electrode active material and a binder is formed on both sides of a negative-electrode charge

collector. As this negative-electrode charge collector, metallic foils, such as copper foil, are used, for example. A dope and the carbon material which can carry out a ** dope are used for a negative-electrode active material in a lithium.

[0025] A scale-like graphite is used although a lithium is specifically later mentioned as a dope and a carbon material which can carry out a ** dope. And in addition to the scale-like graphite which is a negative-electrode active material, and the scale-like graphite concerned, by this gel electrolyte cell, at least one or more kinds of carbon materials are contained among nodular-graphite, massive graphite, fibrous graphite, and difficulty graphitized carbon or carbon black. Moreover, when forming a negative-electrode active material layer using the above negative-electrode active materials, a well-known binder etc. can be added.

[0026] By the way, the binder used for a negative-electrode active material layer does not have lithium occlusion discharge capacity like a negative-electrode active material. Therefore, the increase in the amount of binders will lead to fill deterioration of a negative-electrode active material, and will reduce charge-and-discharge capacity.

[0027] This invention persons could improve the use efficiency of a negative-electrode active material while raising the binding property of a negative-electrode active material layer and a negative-electrode charge collector, without making a binder component increase to the scale-like graphite which is a negative-electrode active material by mixing at least one kind of graphite of other configurations as a result of inquiring wholeheartedly, and they found out that the nonaqueous electrolyte cell which this shows high capacity and a heavy load, and a high cycle property was realizable.

[0028] That is, in addition to the scale-like graphite which is a negative-electrode active material, and the scale-like graphite concerned, by the gel electrolyte cell 1 concerning the gestalt of this operation, at least one or more kinds of carbon materials are contained among nodular-graphite, massive graphite, fibrous graphite, and difficulty graphitized carbon or carbon black.

[0029] As for nodular-graphite and massive graphite, fibrous graphite, and difficulty graphitized carbon, or carbon black, itself has lithium occlusion discharge capacity like a scale-like graphite. [which are mixed in addition to a scale-like graphite] By mixing at least one or more kinds of these carbon materials, the binding property of a negative-electrode active material layer and a negative-electrode charge collector was able to be raised, without making a binder component increase. Furthermore, a suitable, suitable hole will be formed by mixing at least one or more kinds of a carbon material, and it becomes the structure where the dope and ** dope of the lithium ion to the scale-like graphite which is a negative-electrode active material are easy to be performed. The cell in which a heavy load property and a high cycle property are shown can be obtained raising the utilization factor of a scale-like graphite and holding a high charge-and-discharge capacity by this.

[0030] the negative-electrode active material which the amount of nodular-graphite and massive graphite, fibrous graphite, and difficulty graphitized carbon, or carbon black becomes from the one or more above-mentioned kinds of carbon materials mixed with a scale-like graphite -- it is desirable that it is a range below 50 weight sections more than 1 weight section to the whole mixture [which are mixed with the scale-like graphite which is a negative-electrode active material]

[0031] a nodular graphite, a massive graphite, a fibrous graphite, difficulty graphitized carbon, or the amount of mixtures of carbon black -- a negative-electrode active material -- a mixture -- to the whole, if it is under 1 weight section, the effect which raises the adhesion of a negative-electrode charge collector and a negative-electrode active material layer is inadequate, ablation will arise in connection with a long-term charge cycle in the interface of a negative-electrode charge collector and a negative-electrode active material layer, and a cycle property will fall

[0032] moreover, a nodular graphite, a massive graphite, a fibrous graphite, difficulty graphitized carbon, or the amount of mixtures of carbon black -- a negative-electrode active material -- a mixture -- if 50 weight sections are exceeded to the whole, shortly, the rate of the scale-like graphite which is a negative-electrode active material will decrease, and a capacity fall will be caused in addition, a nodular graphite, a massive graphite, a fibrous graphite, difficulty graphitized carbon, or the amount of mixtures of carbon black -- a negative-electrode active material -- a mixture -- if 20 weight sections are exceeded

to the whole, the binding property of a negative-electrode charge collector and a negative-electrode active material layer will not improve greatly any more. Moreover, it becomes a value large enough. [0033] Furthermore, when mixing a nodular graphite or carbon black to a scale-like graphite, since these nodular graphites or the charge-and-discharge capacity per unit weight of carbon black is low as compared with the charge-and-discharge capacity of a scale-like graphite, the effect of the increase in capacity will reduce it by half with rate reduction of a scale-like graphite. Furthermore, since reduction of a scale-like graphite causes the increase in electrode application thickness, this causes reduction of the volume energy density of a cell. Moreover, when mixing difficulty graphitized carbon to a scale-like graphite, although not generated, since a capacity fall shows a gently-sloping discharge curve peculiar to difficulty graphitized carbon, it is not appropriate to use for uses, such as a cellular phone.

[0034] therefore, nodular-graphite and massive graphite, fibrous graphite, and difficulty graphitized carbon or the amount of mixtures of carbon black -- a negative-electrode active material -- a mixture -- while raising the binding property of a negative-electrode active material layer and a negative-electrode charge collector, holding a high charge-and-discharge capacity to the whole by considering as the range below 50 weight sections more than 1 weight section, the use efficiency of a negative-electrode active material can be raised, and a heavy load property and a high cycle property can be realized [to a scale-like graphite] moreover, the more desirable amount of mixtures of nodular-graphite, massive graphite, fibrous graphite, and difficulty graphitized carbon or the amount of mixtures of carbon black -- a negative-electrode active material -- a mixture -- it is a range below 30 weight sections more than 5 weight sections to the whole

[0035] The gel electrolyte layer 4 contains an electrolyte salt, a matrix polymer, and the swelling solvent as a plasticizer.

[0036] independent [in the lithium compound of LiPF_6 , LiBF_4 , $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, or LiCF_3SO_3 grade] as an electrolyte salt -- or it can be mixed and used Also in it, it is desirable to use LiPF_6 from viewpoints, such as ion conductivity.

[0037] Moreover, if the gel electrolyte with which a polymer simple substance or this was used for the matrix polymer shows the ionic conductivity of 1 or more mS/cm at a room temperature, especially chemical structure will not be limited. As this matrix polymer, the compound with which at least one of vinylidene fluoride, acrylonitrile, ethylene oxide, a propylene oxide, or methacrylic nitril is contained as a repeat unit is used. Specifically, poly vinylidene fluoride, a polyacrylonitrile, a polyethylene oxide, a polypropylene oxide, or poly methacrylic nitril is mentioned.

[0038] moreover, independent [in non-aqueous solvents such as ethylene carbonate, propylene carbonate, dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, gamma-butyrolactone, ethyl propyl carbonate, dipropyl carbonate, butyl propyl carbonate, dibutyl carbonate, 1, 2-dimethoxyethane, 1, and 2-diethoxy ethane,] as a swelling solvent -- or it can mix and use

[0039] The electrode winding object 5 is formed by doubling the field which applied the gel electrolyte layer 4, after applying the gel electrolyte layer 4 mentioned above on each one side of such a positive electrode 2 and a negative electrode 3.

[0040] The sheathing film 6 holds the above-mentioned electrode winding object 5. The sheathing film 6 is formed of the sheet-like laminate film of the heat-sealing type which consists of for example, a sheathing protective layer, an aluminum layer, and a heat welding layer (lamination innermost layer).

[0041] Here, plastic film etc. can be mentioned as the quality of the material of a heat welding layer and an external protective layer. Although polyethylene, polypropylene, nylon (tradename), etc. are used for the plastic film which forms a heat welding layer, if it is thermoplastic plastic material, the raw material will not be asked.

[0042] Without making a binder component increase to the scale-like graphite which is a negative-electrode active material by mixing at least one kind of graphite of other configurations, as for the gel electrolyte cell 1 concerning a gestalt of this operation which was mentioned above, the binding property of a negative-electrode active material layer and a negative-electrode charge collector can both raise the use efficiency of a negative-electrode active material as it is high, and thereby, it shows high capacity and a heavy load, and a high cycle property.

[0043] And the gel electrolyte cell 1 concerning a gestalt of this operation which was mentioned above is manufactured as follows.

[0044] first, the positive electrode which contains a positive active material and a binder as a positive electrode 2 -- in a mixture, by [used as a positive-electrode charge collector] applying and drying uniformly, for example on metallic foils, such as an aluminum foil, a positive-active-material layer is formed and a positive-electrode sheet is produced the above-mentioned positive electrode -- and also it can use a well-known binder as a binder of a mixture -- the above-mentioned positive electrode -- a well-known additive etc. can be added to a mixture

[0045] Next, a positive-electrode sheet is cut down to band-like. And lead wire is welded to the agenesis portion of a positive-active-material layer, and it considers as the positive-electrode terminal 7.

Aluminum, titanium, or these alloys are mentioned as an example of the material used for the positive-electrode terminal 7. Thus, the band-like positive electrode 2 is obtained.

[0046] moreover, the negative electrode in which a negative electrode 3 contains a negative-electrode active material and a binder -- in a mixture, by [used as a negative-electrode charge collector] applying and drying uniformly, for example on metallic foils, such as copper foil, a negative-electrode active material layer is formed and a negative-electrode sheet is produced here -- this negative electrode -- the scale-like graphite which is a negative-electrode active material at a mixture, and the scale-like graphite concerned -- in addition, the negative-electrode active material which consists of at least one or more kinds of carbon materials among nodular-graphite, massive graphite, fibrous graphite, and difficulty graphitized carbon or carbon black -- a mixture is used moreover, the above-mentioned negative electrode -- and also it can use a well-known binder as a binder of a mixture -- the above-mentioned negative electrode -- a well-known additive etc. can be added to a mixture

[0047] Next, a negative-electrode sheet is cut down to band-like. And lead wire is welded to the agenesis portion of the negative-electrode active material layer of a negative-electrode charge collector, and it considers as the negative-electrode terminal 8. Copper, nickel, or these alloys are mentioned as an example of the material used for the negative-electrode terminal 8. Thus, the band-like negative electrode 3 is obtained.

[0048] Next, the gel electrolyte layer 4 is formed on a positive-active-material layer and a negative-electrode active material layer. In order to form the gel electrolyte layer 4, first, an electrolyte salt is dissolved in a non-aqueous solvent, and nonaqueous electrolyte is produced. And a matrix polymer is added to this nonaqueous electrolyte, it stirs well, a matrix polymer is dissolved, and a sol-like electrolytic solution is obtained.

[0049] Next, the specified quantity application of this electrolytic solution is carried out on a positive-active-material layer and a negative-electrode active material. Then, by cooling at a room temperature, a matrix polymer gels and the gel electrolyte layer 4 is formed on a positive-active-material layer and a negative-electrode active material.

[0050] And the band-like positive electrode 2 and band-like negative electrode 3 which were produced as mentioned above are made to rival through the gel electrolyte layer 4, are pressed, and let them be an electrode layered product. Furthermore, this electrode layered product is wound around a longitudinal direction, and it considers as the electrode winding object 5.

[0051] While inserting this electrode winding object 5 into the last with the sheathing film 6 which consists of an insulating material, and obturating the periphery marginal part of the sheathing film 6 at it and putting the positive-electrode terminal 7 and the negative-electrode terminal 8 between it at the obturation section of the sheathing film 6, the electrode winding object 5 is sealed in the sheathing film 6. Furthermore, it heat-treats to the electrode winding object 5 in the state where it packed with the sheathing film 6. The gel electrolyte cell 1 is completed as mentioned above.

[0052] In addition, although the case where carried out the laminating of the band-like positive electrode 2 and the band-like negative electrode 3, and wound around the longitudinal direction further and it considered as the electrode winding object 6 was mentioned as the example and the gestalt of operation mentioned above explained it, this invention is not limited to this, and when the laminating of the rectangle-like positive electrode 2 and the rectangle-like negative electrode 3 was carried out and being

considered as the electrode layered product, or when an electrode layered product is folded up by turns, it can be applied.

[0053] Moreover, although the gel electrolyte cell 1 which used the gel electrolyte was mentioned as the example and the gestalt of operation mentioned above explained it as a nonaqueous electrolyte cell, this invention is not limited to this and can be applied also about the nonaqueous electrolyte cell using nonaqueous electrolyte, and the solid electrolyte cell using the solid electrolyte which does not contain a swelling solvent.

[0054] Furthermore, the nonaqueous electrolyte cell concerning this invention is not limited especially about the configuration, and can make a sheet type, cylindrical, a square shape, a coin type, etc. a thin shape and the various sizes of large-sized **. Moreover, this invention is [primary cell] applicable also about a rechargeable battery.

[0055]

[Example] Next, it is a book.

[0056] <Example 1> The negative electrode was produced as follows first.

[0057] the negative-electrode active material which serves as [nodular graphite] 99 weight sections from the powder which mixed 1 weight section in the ground scale-like graphite which is a negative-electrode active material -- a mixture -- as 90 weight sections and a binder -- poly (vinylidene fluoride-co-hexafluoropropylene) -- 10 weight sections -- mixing -- a negative electrode -- prepared the mixture, the N-methyl-2-pyrrolidone was made to distribute this further, and it considered as the shape of a slurry And this slurry was uniformly applied to both sides of band-like copper foil with a thickness of 20 micrometers which is a negative-electrode charge collector, compression molding was carried out with the roll-press machine after dryness, and the negative electrode was produced. In addition, the lead wire made from nickel was welded to the agensis portion of the negative-electrode active material layer of a negative-electrode charge collector, and it considered as the negative-electrode terminal.

[0058] Moreover, the positive electrode was produced as follows.

[0059] First, a lithium carbonate and cobalt carbonate were mixed at a rate of 0.5:1 by the mole ratio, it calcinated at 900 degrees C among air for 5 hours, and LiCoO₂ used as a positive active material was obtained.

[0060] next, obtained LiCoO₂ -- as 91 weight sections and an electric conduction agent -- a graphite -- as 6 weight sections and a binder -- poly (vinylidene fluoride-co-hexafluoropropylene) -- 10 weight sections -- mixing -- a positive electrode -- prepared the mixture, the N-methyl-2-pyrrolidone was made to distribute this further, and it considered as the shape of a slurry And this slurry was uniformly applied to both sides of a band-like aluminum foil with a thickness of 20 micrometers which is a positive-electrode charge collector, compression molding was carried out with the roll-press machine after dryness, and the positive electrode was produced. In addition, the lead wire made from aluminum was welded to the agensis portion of the positive-active-material layer of a positive-electrode charge collector, and it considered as the positive-electrode terminal.

[0061] Next, the gel electrolyte layer was obtained as follows.

[0062] First, propylene carbonate was mixed for ethylene carbonate with the 42.5 weight sections, 15 weight sections were mixed with the 42.5 weight sections for LiPF₆, and the plasticizer was prepared. In 30 weight sections of this plasticizer, 60 weight sections were mixed [poly (vinylidene fluoride-co-hexafluoropropylene)] with 10 weight sections for dimethyl carbonate, and the electrolytic solution was prepared in them.

[0063] On the positive-active-material layer and the negative-electrode active material layer, this electrolytic solution is applied uniformly, and was infiltrated, it was left in ordinary temperature for 8 hours, dimethyl carbonate was evaporated and removed, and the gel electrolyte layer was obtained.

[0064] And the 5cmx4cmx0.4cm electrode winding object was acquired by making the side in which the gel electrolyte layer was formed in the positive electrode produced as mentioned above and the negative electrode counter, and winding around lamination and a longitudinal direction.

[0065] The gel electrolyte cell was obtained by sealing this electrode winding object in the laminate film which consists of a three-tiered structure of polypropylene / aluminum / nylon. In addition, the positive-

electrode terminal and the negative-electrode terminal were put between the obturation section of a sheathing film at this time.

[0066] <an example 2> -- a negative-electrode active material -- except 95:5 having carried out comparatively the ratio of the scale-like graphite and nodular graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0067] <an example 3> -- a negative-electrode active material -- except 80:20 having carried out comparatively the ratio of the scale-like graphite and nodular graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0068] <an example 4> -- a negative-electrode active material -- except 70:30 having carried out comparatively the ratio of the scale-like graphite and nodular graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0069] <an example 5> -- a negative-electrode active material -- except 60:40 having carried out comparatively the ratio of the scale-like graphite and nodular graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0070] <an example 6> -- a negative-electrode active material -- except 50:50 having carried out comparatively the ratio of the scale-like graphite and nodular graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0071] <an example 7> -- a nodular graphite -- replacing with -- a massive graphite -- using -- a negative-electrode active material -- except 80:20 having carried out comparatively the ratio of the scale-like graphite and massive graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0072] <an example 8> -- a nodular graphite -- replacing with -- a massive graphite -- using -- a negative-electrode active material -- except 60:40 having carried out comparatively the ratio of the scale-like graphite and massive graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0073] <an example 9> -- a nodular graphite -- replacing with -- a fibrous graphite -- using -- a negative-electrode active material -- except 80:20 having carried out comparatively the ratio of the scale-like graphite and fibrous graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0074] <an example 10> -- a nodular graphite -- replacing with -- difficulty graphitized carbon -- using -- a negative-electrode active material -- except 80:20 having carried out comparatively the ratio of the scale-like graphite and difficulty graphitized carbon which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0075] <an example 11> -- a nodular graphite -- replacing with -- carbon black -- using -- a negative-electrode active material -- except 80:20 having carried out comparatively the ratio of the scale-like graphite and carbon black which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0076] <an example 12> -- the negative-electrode active material with which it comes to mix a scale-like graphite, a nodular graphite, and carbon black by the ratio of 80:15:5 -- except having used the mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0077] <an example 13> -- the negative-electrode active material with which it comes to mix a scale-like graphite, a nodular graphite, and a fibrous graphite by the ratio of 80:15:5 -- except having used the mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0078] <Example 1 of comparison> Except having used only the scale-like graphite as a negative-

electrode active material, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode.

[0079] <the example 2 of comparison> -- a negative-electrode active material -- except 99.5:0.5 having carried out comparatively the ratio of the scale-like graphite and nodular graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0080] <the example 3 of comparison> -- a negative-electrode active material -- except 30:70 having carried out comparatively the ratio of the scale-like graphite and nodular graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0081] <Example 4 of comparison> Except having used only the nodular graphite as a negative-electrode active material, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode.

[0082] <the example 5 of comparison> -- a nodular graphite -- replacing with -- a massive graphite -- using -- a negative-electrode active material -- except 40:60 having carried out comparatively the ratio of the scale-like graphite and massive graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0083] <the example 6 of comparison> -- a nodular graphite -- replacing with -- a fibrous graphite -- using -- a negative-electrode active material -- except 40:60 having carried out comparatively the ratio of the scale-like graphite and fibrous graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0084] <the example 7 of comparison> -- a nodular graphite -- replacing with -- difficulty graphitized carbon -- using -- a negative-electrode active material -- except 40:60 having carried out comparatively the ratio of the scale-like graphite and difficulty graphitized carbon which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0085] <the example 8 of comparison> -- a nodular graphite -- replacing with -- carbon black -- using -- a negative-electrode active material -- except 40:60 having carried out comparatively the ratio of the scale-like graphite and carbon black which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0086] <the example 9 of comparison> -- the negative-electrode active material with which it comes to mix a scale-like graphite, a nodular graphite, and carbon black by the ratio of 40:40:20 -- except having used the mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0087] And about the gel electrolyte cell produced as mentioned above, the peel strength between negative-electrode charge collector-negative-electrode active material layers and the service capacity of a negative-electrode active material were measured, and the characterization examination of the load characteristic about the produced gel electrolyte cell and a cycle property was performed further.

[0088] The peel strength between negative-electrode charge collector-negative-electrode active material layers was measured by the so-called T character friction test.

[0089] As shown in drawing 4, the T character friction test stuck the adhesive tape 10 on the negative-electrode active material layer 3a front face of the negative electrode 3 with a width of face [of 30mm], and a length of 200mm, stuck this negative-electrode charge collector 3b side on the stainless steel board 11 further, and fixed A portion in drawing 4. This part was removed and it removed 10cm by pulling the removed edge to the stainless steel board 11 in the horizontal direction of drawing 4 Nakaya mark B, i.e., the direction. The average of the force required at this time was made into peel strength.

[0090] the negative-electrode active material same about the service capacity of a negative-electrode active material -- the coin type cell 20 as shown in drawing 5 using a mixture was produced, and it evaluated using this coin type cell 20

[0091] the negative electrode first obtained like an above-mentioned method as the creation method of the coin type cell 20 -- the mixture was applied on the nickel mesh (20 micrometers of diameters of

nickel fiber) used as a charge collector, it dried and the negative-electrode active material layer was formed. And the nickel mesh in which the negative-electrode active material layer was formed was used as the pellet-like negative electrode 21 by piercing to disc-like [with a diameter of 15.5mm].

[0092] Moreover, it considered as the positive electrode 22 by piercing a lithium metallic foil to a negative electrode and abbreviation isomorphism.

[0093] Moreover, nonaqueous electrolyte was prepared by dissolving LiPF₆ by the concentration of 1 mol/l into the amount mixed solvent of isochores of ethylene carbonate and propylene carbonate.

[0094] The negative electrode 21 obtained as mentioned above was held in the negative-electrode can 23, the positive electrode 22 was held in the positive-electrode can 24, and the separator 25 which consists of a porous membrane made from polypropylene between a positive electrode 22 and a negative electrode 21 was allotted. the inside of the positive-electrode can 24 and the negative-electrode can 23 -- nonaqueous electrolyte -- pouring in -- the positive-electrode can 24 and the negative-electrode can 23 -- an insulating gasket 26 -- minding -- the coin type cell 20 whose thickness a diameter is 20mm and is 2.5mm was produced by fixing in total

[0095] And about the obtained coin type cell 20, 10 hour-rate charge of geometric capacity was performed to minimum 0V by constant-voltage constant-current charge, and, next, 10 hour-rate constant-current discharge was performed among final-voltage 1.5V. Service capacity at this time was made into the service capacity of a negative-electrode active material.

[0096] As a load characteristic, about the gel electrolyte cell, 1 / 3 hour-rate electric discharge of geometric capacity (3C) were performed first, and it evaluated as follows. First, to each cell, 23 degrees C and constant-current constant-potential charge were performed to 4.2V for 10 hours, next, constant-current discharge of 3C was performed among final-voltage 3.2V, and service capacity was determined. And the output in each hour-rate electric discharge was computed as 100 molar fractions to 1/5C from the average voltage called for from now on. Moreover, the volume energy density of the cell to the service capacity at this time was computed.

[0097] As a cycle property, to each cell, constant-current constant-potential charge was performed to upper limit 4.2V at 23 degrees C, next constant-current discharge of 2 hour-rate electric discharge (1/2C) of geometric capacity was performed among final-voltage 3.2V. It is 500 cycle *****, using this as 1 cycle. And the output in hour-rate electric discharge was computed from the average voltage called for from now on as 100 molar fractions to 1/5C in early stages of a cycle (the 1st cycle eye).

[0098] Each cell characterization result about the cell of an example 1 - an example 13, the example 1 of comparison - the example 9 of comparison is shown in Table 1.

[0099]

[Table 1]

	添加炭素材料 種類	炭素材料添 量(Wt%)	負極厚み (μm)	負極剝離 強度(g/mm)	放電容量 (mAh/g)	負荷特性 (%)	3C放電のI _比 キ 密度(WA/l)	サイクル 特性(%)
実施例1	球状黒鉛	1	100	9.4	358	70	321	66
実施例2	球状黒鉛	5	103	15.6	358	76	338	78
実施例3	球状黒鉛	20	108	20.3	352	82	360	83
実施例4	球状黒鉛	30	109	24.8	350	81	364	83
実施例5	球状黒鉛	40	115	23.6	348	83	350	84
実施例6	球状黒鉛	50	121	23.3	343	84	326	87
実施例7	塊状黒鉛	20	105	16.2	352	80	338	81
実施例8	塊状黒鉛	40	106	18.2	352	78	342	80
実施例9	繊維状黒鉛	20	106	14.6	370	72	332	65
実施例10	難黒鉛化炭素	20	126	15.3	378	76	301	70
実施例11	カーボンブラック	20	106	11.2	348	74	322	50
実施例12	球状黒鉛+カーボンブラック	15+5	106	19.4	345	76	327	77
実施例13	球状黒鉛+繊維状黒鉛	15+5	107	21.8	355	78	342	79
比較例1	—	0	100	3.3	360	34	168	33
比較例2	球状黒鉛	0.5	100	3.2	360	35	163	32
比較例3	球状黒鉛	70	125	24.3	338	86	320.2	88
比較例4	球状黒鉛	100	140	24.3	330	89	295	90
比較例5	塊状黒鉛	60	123	16.9	344	81	312	81
比較例6	繊維状黒鉛	60	124	17.8	350	78	314	79
比較例7	難黒鉛化炭素	60	126	15.3	378	76	301	70
比較例8	カーボンブラック	60	130	10.7	327	74	264	49
比較例9	球状黒鉛+カーボンブラック	40+20	131	22.1	335	76	271	76

[0100] First, when it sees about the peel strength between negative-electrode charge collector-negative-electrode active material layers, in the example 2 of comparison whose example 1 of comparison and addition which did not add a carbon material are 0.5 % of the weight, peel strength is extremely low and

it turns out that a negative-electrode active material layer tends to exfoliate from a negative-electrode charge collector. Although peel strength also increases with the increase in the rate of the added carbon material, even if it will be saturated if the rate of a carbon material becomes about 20% of the weight and the addition rate of a carbon material increases after it, most improvement in peel strength is not found.

[0101] Moreover, the cycle property of a cell is also known by that the good value is acquired, so that the peel strength between negative-electrode charge collector-negative-electrode active material layers becomes large.

[0102] On the other hand, the rate of a negative-electrode active material will fall and service capacity will fall as the addition rate of a carbon material increases. Moreover, although the improvement effect is notably seen to about 5 % of the weight, if the addition rate of a carbon material becomes more than it also about a load characteristic, the property of an addition carbon material will come to appear strongly, and the improvement effect of a load characteristic will no longer be seen so much.

[0103] Moreover, the thickness of a negative electrode is thick and a bird clapper is known as the addition of a carbon material increases, when it is going to make equal service capacity per unit area of a cell. This means reducing the volume energy density of a cell by adding a carbon material. About the volume energy density at the time of 3C electric discharge, when the additions of a carbon material are 5 % of the weight or more and 30 % of the weight or less, it turns out that the good value is acquired.

[0104] When the addition of the carbon material added from the above result to the scale-like graphite which is a negative-electrode active material is made into 1 % of the weight or more and 50% of the weight of the range, it turns out that the desirable result is obtained. Also in it, when the addition of a carbon material is made into 5 % of the weight or more and 30% of the weight or less of the range, it turns out that the desirable result is obtained especially.

[0105]

[Effect of the Invention] In this invention, while raising the binding property of a negative-electrode active material layer and a negative-electrode charge collector, without making the scale-like graphite which is a negative-electrode active material increase a binder component by mixing at least one or more kinds of carbon material among nodular-graphite, massive graphite, fibrous graphite, and difficulty graphitized carbon or carbon black, the use efficiency of a negative-electrode active material can be raised, and the nonaqueous electrolyte cell which has high capacity and a heavy load, and a high cycle property can be realized.

[Translation done.]

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to a nonaqueous electrolyte cell.

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PRIOR ART

[Description of the Prior Art] In recent years, cordless-izing including electronic equipment, such as a cellular phone and a book type personal computer, and portable-ization progress, and a thin shape and small and lightweight pocket electronic equipment are developed one after another. Moreover, the amount of the power used increases by diversification of a device, and the need over high-capacity-izing of the cell which is the energy source of these electronic equipment, especially a rechargeable battery is increasing.

[0003] There are a lead accumulator and a nickel-cadmium battery as a rechargeable battery used from the former, and the nickel hydride battery and the lithium ion battery are put in practical use as a new rechargeable battery. However, since these rechargeable batteries were using the liquefied electrolyte as an electrolyte, they had the problem of the liquid spill from a cell. Then, the solid electrolyte rechargeable lithium-ion battery which used as an electrolyte the macromolecule gel swollen by the electrolytic solution was developed that such a problem should be solved. By development of this solid electrolyte rechargeable lithium-ion battery, worries about the liquid spill from a cell disappeared, and development of the rechargeable battery which are small, lightweight, and a thin shape and has a high energy density was attained.

[0004] If the composition of the above-mentioned solid electrolyte rechargeable lithium-ion battery is explained, the positive-active-material layer containing LiCoO_2 and a graphite is formed on the positive-electrode charge collector which consists of aluminum sheet metal, and the positive electrode is constituted. Moreover, on the negative-electrode charge collector which consists of copper sheet metal, the negative-electrode active material layer containing carbon, corks, graphite, etc. is formed, and the negative electrode is constituted.

[0005] It consists of polypropylene, polyethylene, etc. between a positive electrode and a negative electrode, and the separator which is the thin film which has pore is incorporated. And between these electrodes and separator, the sandwich structure with which the gel electrolyte made to swell a polyacrylonitrile (PAN), a polyethylene oxide (PEO), and a macromolecule like a polyvinylidene fluoride (PVDF) by the electrolytic solution containing lithium salt was filled up is taken. Moreover, the packaging of these unit cells (unit cell) that became a sandwich structure is carried out to a metal thin film like an aluminum foil as a container for enclosure by the enclosure material which consisted of plastic film, such as nylon, polyethylene, polypropylene, and a polyethylene terephthalate.

[0006] When it furthermore sees about a negative-electrode active material, there is restoration nature how a lot of graphites can be stuffed in limited volume called a cell with the lithium occlusion of the graphite itself and discharge capacity. If this is not only a graphite but powder, it will be greatly influenced by the configuration. When the configuration of the powder of a graphite is considered, the shape of a globular shape, mass, and a scale and fibrous ** are mentioned.

[0007] Usually, a solid electrolyte negative electrode is although the mixture of a graphite and a binder is applied to both sides of the metal thin film which is a charge collector, or one side, this is rolled out suitably and it is formed. Among the graphites of each above-mentioned configuration, according to the feature that a particle carries out orientation of the scale-like graphite in the same direction with rolling,

close nature is large and it can be said that it is the material restoration nature also excelled [material] in the scale-like graphite most as a negative-electrode material of the graphite origin from large next doors and these points.

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EFFECT OF THE INVENTION

[Effect of the Invention] While raising the binding property of a negative-electrode active material layer and a negative-electrode charge collector to the scale-like graphite which is a negative-electrode active material by this invention by mixing at least one or more kinds of carbon material among nodular-graphite, massive graphite, fibrous graphite, and difficulty graphitized carbon or carbon black, without making a binder component increase. The use efficiency of a negative-electrode active material can be raised, and the nonaqueous electrolyte cell which has high capacity and a heavy load, and a high cycle property can be realized.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, when using a scale-like graphite as a negative-electrode active material, there is a problem which must be solved. Since a scale-like graphite has the large stacking tendency, although restoration nature goes up in the first place with rolling. Conversely, the cell reaction which was an electrode surface portion since an electrolyte did not permeate the interior of an electrode when restoration nature goes up too much, the hole portion in an electrode is restricted and the electrode of a cell is formed is not performed. The technical problem are not suitable for the decline in a reaction utilization factor or heavy load electric discharge of an electrode arises (JP, 8-287952, A).

[0009] In the cell especially using the gel electrolyte, in order to solve the above technical problems, it is needed for the gel electrolyte itself to permeate into an electrode. Since viscosity is very high as compared with the liquid system electrolyte of the former [electrolyte / gel], osmosis into an electrode paint film cannot take place easily. Therefore, it compares with the case of the liquid system electrolyte which will be solved if only osmosis of the electrolytic solution is taken into consideration, and it becomes much more important to secure the suitable hole in an electrode.

[0010] When only a scale-like graphite is used for the second as a negative-electrode active material and an electrode is formed in it, by expansion contraction at the time of an active material repeating [the binding property between a charge collector and an active material] charge and discharge as compared with them, such as a nodular graphite, for a low reason etc., ablation of the active material from an electrode arises and a cycle property falls. The problem of making a binder component increase, in order to prevent this making the charge-and-discharge capacity of an electrode fall as a result arises.

[0011] this invention is proposed in view of such the conventional actual condition, and it has high capacity and a high cycle property using the scale-like graphite which has service capacity high as a negative-electrode active material, and aims at offering the nonaqueous electrolyte cell using the negative electrode and it which show a high volume energy density also in high current electric discharge.

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MEANS

[Means for Solving the Problem] the negative-electrode active material which the negative electrode of this invention becomes from at least one or more kinds of carbon materials among scale-like graphite [which is a negative-electrode active material], nodular-graphite and massive graphite, fibrous graphite, and difficulty graphitized carbon, or carbon black -- a mixture -- containing -- the negative-electrode active material concerned -- a mixture is characterized by containing the one or more above-mentioned kinds of carbon materials in 1 % of the weight or more and 50% of the weight or less of the range [0013] In the negative electrode concerning this invention which was mentioned above, since the graphite of other configurations of nodular-graphite, massive graphite, fibrous graphite, and difficulty graphitized carbon or carbon black is mixed by the scale-like graphite which is a negative-electrode active material, while raising the binding property of a negative-electrode active material layer and a negative-electrode charge collector, without making a binder component increase, the use efficiency of a negative-electrode active material improves.

[0014] Moreover, the nonaqueous electrolyte cell of this invention is equipped with the nonaqueous electrolyte which intervenes between the positive electrode which has the positive active material in which a dope and a ** dope of a lithium are possible, the negative electrode which has the negative-electrode active material in which a dope and a ** dope of a lithium are possible, and a positive electrode and a negative electrode. and the negative-electrode active material which the above-mentioned negative electrode becomes from at least one or more kinds of carbon materials among scale-like graphite [whose nonaqueous electrolyte cell of this invention is a negative-electrode active material], nodular-graphite and massive graphite, fibrous graphite, and difficulty graphitized carbon, or carbon black -- a mixture -- containing -- the negative-electrode active material concerned -- a mixture is characterized by containing the one or more above-mentioned kinds of carbon materials in 1 % of the weight or more and 50% of the weight or less of the range

[0015] By the nonaqueous electrolyte cell concerning this invention which was mentioned above, while raising the binding property of a negative-electrode active material layer and a negative-electrode charge collector even if it does not make a binder component increase since the graphite of other configurations of nodular-graphite, massive graphite, fibrous graphite, and difficulty graphitized carbon or carbon black is mixed by the scale-like graphite which is a negative-electrode active material, the use efficiency of a negative-electrode active material improves. And the nonaqueous electrolyte cell concerning this invention using such a negative electrode has high capacity and a heavy load, and a high cycle property.

[0016]

[Embodiments of the Invention] Hereafter, the gestalt of operation of this invention is explained.

[0017] The example of 1 composition of the gel electrolyte cell 1 concerning the gestalt of this operation is shown in drawing 1 and drawing 2 . This gel electrolyte cell 1 is equipped with the gel electrolyte layer 4 formed on the band-like positive electrode 2, the band-like negative electrode 3 which countered with the positive electrode 2 and was allotted, and a positive electrode 2 and a negative electrode 3.

[0018] And this gel electrolyte cell 1 is covered with the sheathing film 6 with which the electrode winding object 5 which was wound around the longitudinal direction, and which is shown in drawing 3

consists of an insulating material, and is sealed while the laminating of the positive electrode 2 in which the gel electrolyte layer 4 was formed, and the negative electrode 3 in which the gel electrolyte layer 4 was formed is carried out. And the positive-electrode terminal 7 is connected to a positive electrode 2, the negative-electrode terminal 8 is connected to the negative electrode 3, respectively, and these positive-electrode terminals 7 and negative-electrode terminals 8 are put between the obturation section which is the periphery section of the sheathing film 6.

[0019] The positive-active-material layer in which a positive electrode 2 contains a positive active material is formed on both sides of a positive-electrode charge collector. As this positive-electrode charge collector, metallic foils, such as an aluminum foil, are used, for example.

[0020] As a positive active material, a metallic oxide, metallic sulfide, or a specific macromolecule can be used according to the kind of cell made into the purpose.

[0021] For example, when considering as the lithium cell using the dissolution and the deposit of a lithium, macromolecules, such as metallic sulfide which does not contain the lithium of TiS_2 , MoS_2 , NbSe_2 , and V_2O_5 grade or an oxide and also a polyacetylene, and polypyrrole, can also be used.

[0022] When considering as the lithium ion battery using the dope and the ** dope of a lithium ion, the lithium multiple oxide which makes a subject Li_xMO_2 (the inside M of a formula expresses the transition metals more than a kind, and x changes with charge-and-discharge states of a cell, and it is usually 0.05 [or more] and 1.10 or less.) can be used. As transition metals M which constitute this lithium multiple oxide, Co, nickel, Mn, etc. are desirable. as the example of such a lithium multiple oxide -- LiCoO_2 , LiNiO_2 , and $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$ (it is $0 < y < 1$ among a formula.), and LiMn_2O_4 , LiMPO_4 (M expresses the transition metals more than kinds, such as Fe, among a formula), etc. can be mentioned One kind may be independently used for these lithium multiple oxides, and two or more sorts may be mixed and used for them.

[0023] A lithium multiple oxide can generate the high voltage and serves as a positive active material which was excellent in energy density. You may use two or more sorts of these positive active materials for a positive active material collectively. Moreover, when forming a positive-active-material layer using the above positive active materials, a well-known electric conduction agent, a well-known binder, etc. can be added.

[0024] Moreover, the negative-electrode active material layer in which a negative electrode 3 contains a negative-electrode active material and a binder is formed on both sides of a negative-electrode charge collector. As this negative-electrode charge collector, metallic foils, such as copper foil, are used, for example. A dope and the carbon material which can carry out a ** dope are used for a negative-electrode active material in a lithium.

[0025] A scale-like graphite is used although a lithium is specifically later mentioned as a dope and a carbon material which can carry out a ** dope. And in addition to the scale-like graphite which is a negative-electrode active material, and the scale-like graphite concerned, by this gel electrolyte cell, at least one or more kinds of carbon materials are contained among nodular-graphite, massive graphite, fibrous graphite, and difficulty graphitized carbon or carbon black. Moreover, when forming a negative-electrode active material layer using the above negative-electrode active materials, a well-known binder etc. can be added.

[0026] By the way, the binder used for a negative-electrode active material layer does not have lithium occlusion discharge capacity like a negative-electrode active material. Therefore, the increase in the amount of binders will lead to fill deterioration of a negative-electrode active material, and will reduce charge-and-discharge capacity.

[0027] This invention persons could improve the use efficiency of a negative-electrode active material while raising the binding property of a negative-electrode active material layer and a negative-electrode charge collector, without making a binder component increase to the scale-like graphite which is a negative-electrode active material by mixing at least one kind of graphite of other configurations as a result of inquiring wholeheartedly, and they found out that the nonaqueous electrolyte cell which this shows high capacity and a heavy load, and a high cycle property was realizable.

[0028] That is, in addition to the scale-like graphite which is a negative-electrode active material, and

the scale-like graphite concerned, by the gel electrolyte cell 1 concerning the gestalt of this operation, at least one or more kinds of carbon materials are contained among nodular-graphite, massive graphite, fibrous graphite, and difficulty graphitized carbon or carbon black.

[0029] As for nodular-graphite and massive graphite, fibrous graphite, and difficulty graphitized carbon, or carbon black, itself has lithium occlusion discharge capacity like a scale-like graphite. [which are mixed in addition to a scale-like graphite] By mixing at least one or more kinds of these carbon materials, the binding property of a negative-electrode active material layer and a negative-electrode charge collector was able to be raised, without making a binder component increase. Furthermore, a suitable, suitable hole will be formed by mixing at least one or more kinds of a carbon material, and it becomes the structure where the dope and ** dope of the lithium ion to the scale-like graphite which is a negative-electrode active material are easy to be performed. The cell in which a heavy load property and a high cycle property are shown can be obtained raising the utilization factor of a scale-like graphite and holding a high charge-and-discharge capacity by this.

[0030] the negative-electrode active material which the amount of nodular-graphite and massive graphite, fibrous graphite, and difficulty graphitized carbon, or carbon black becomes from the one or more above-mentioned kinds of carbon materials mixed with a scale-like graphite -- it is desirable that it is a range below 50 weight sections more than 1 weight section to the whole mixture [which are mixed with the scale-like graphite which is a negative-electrode active material]

[0031] a nodular graphite, a massive graphite, a fibrous graphite, difficulty graphitized carbon, or the amount of mixtures of carbon black -- a negative-electrode active material -- a mixture -- to the whole, if it is under 1 weight section, the effect which raises the adhesion of a negative-electrode charge collector and a negative-electrode active material layer is inadequate, ablation will arise in connection with a long-term charge cycle in the interface of a negative-electrode charge collector and a negative-electrode active material layer, and a cycle property will fall

[0032] moreover, a nodular graphite, a massive graphite, a fibrous graphite, difficulty graphitized carbon, or the amount of mixtures of carbon black -- a negative-electrode active material -- a mixture -- if 50 weight sections are exceeded to the whole, shortly, the rate of the scale-like graphite which is a negative-electrode active material will decrease, and a capacity fall will be caused in addition, a nodular graphite, a massive graphite, a fibrous graphite, difficulty graphitized carbon, or the amount of mixtures of carbon black -- a negative-electrode active material -- a mixture -- if 20 weight sections are exceeded to the whole, the binding property of a negative-electrode charge collector and a negative-electrode active material layer will not improve greatly any more Moreover, it becomes a value large enough.

[0033] Furthermore, when mixing a nodular graphite or carbon black to a scale-like graphite, since these nodular graphites or the charge-and-discharge capacity per unit weight of carbon black is low as compared with the charge-and-discharge capacity of a scale-like graphite, the effect of the increase in capacity will reduce it by half with rate reduction of a scale-like graphite. Furthermore, since reduction of a scale-like graphite causes the increase in electrode application thickness, this causes reduction of the volume energy density of a cell. Moreover, when mixing difficulty graphitized carbon to a scale-like graphite, although not generated, since a capacity fall shows a gently-sloping discharge curve peculiar to difficulty graphitized carbon, it is not appropriate to use for uses, such as a cellular phone.

[0034] therefore, nodular-graphite and massive graphite, fibrous graphite, and difficulty graphitized carbon or the amount of mixtures of carbon black -- a negative-electrode active material -- a mixture -- while raising the binding property of a negative-electrode active material layer and a negative-electrode charge collector, holding a high charge-and-discharge capacity to the whole by considering as the range below 50 weight sections more than 1 weight section, the use efficiency of a negative-electrode active material can be raised, and a heavy load property and a high cycle property can be realized [to a scale-like graphite] moreover, the more desirable amount of mixtures of nodular-graphite, massive graphite, fibrous graphite, and difficulty graphitized carbon or the amount of mixtures of carbon black -- a negative-electrode active material -- a mixture -- it is a range below 30 weight sections more than 5 weight sections to the whole

[0035] The gel electrolyte layer 4 contains an electrolyte salt, a matrix polymer, and the swelling solvent

as a plasticizer.

[0036] independent [in the lithium compound of LiPF_6 , LiBF_4 , $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, or LiCF_3SO_3 grade] as an electrolyte salt -- or it can be mixed and used Also in it, it is desirable to use LiPF_6 from viewpoints, such as ion conductivity.

[0037] Moreover, if the gel electrolyte with which a polymer simple substance or this was used for the matrix polymer shows the ionic conductivity of 1 or more mS/cm at a room temperature, especially chemical structure will not be limited. As this matrix polymer, the compound with which at least one of vinylidene fluoride, acrylonitrile, ethylene oxide, a propylene oxide, or methacrylic nitril is contained as a repeat unit is used. Specifically, poly vinylidene fluoride, a polyacrylonitrile, a polyethylene oxide, a polypropylene oxide, or poly methacrylic nitril is mentioned.

[0038] moreover, independent [in non-aqueous solvents such as ethylene carbonate, propylene carbonate, dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, gamma-butyrolactone, ethyl propyl carbonate, dipropyl carbonate, butyl propyl carbonate, dibutyl carbonate, 1, 2-dimethoxyethane, 1, and 2-diethoxy ethane,] as a swelling solvent -- or it can mix and use

[0039] The electrode winding object 5 is formed by doubling the field which applied the gel electrolyte layer 4, after applying the gel electrolyte layer 4 mentioned above on each one side of such a positive electrode 2 and a negative electrode 3.

[0040] The sheathing film 6 holds the above-mentioned electrode winding object 5. The sheathing film 6 is formed of the sheet-like laminate film of the heat-sealing type which consists of for example, a sheathing protective layer, an aluminum layer, and a heat welding layer (lamination innermost layer).

[0041] Here, plastic film etc. can be mentioned as the quality of the material of a heat welding layer and an external protective layer. Although polyethylene, polypropylene, nylon (tradename), etc. are used for the plastic film which forms a heat welding layer, if it is thermoplastic plastic material, the raw material will not be asked.

[0042] Without making a binder component increase to the scale-like graphite which is a negative-electrode active material by mixing at least one kind of graphite of other configurations, as for the gel electrolyte cell 1 concerning a gestalt of this operation which was mentioned above, the binding property of a negative-electrode active material layer and a negative-electrode charge collector can both raise the use efficiency of a negative-electrode active material as it is high, and thereby, it shows high capacity and a heavy load, and a high cycle property.

[0043] And the gel electrolyte cell 1 concerning a gestalt of this operation which was mentioned above is manufactured as follows.

[0044] first, the positive electrode which contains a positive active material and a binder as a positive electrode 2 -- in a mixture, by [used as a positive-electrode charge collector] applying and drying uniformly, for example on metallic foils, such as an aluminum foil, a positive-active-material layer is formed and a positive-electrode sheet is produced the above-mentioned positive electrode -- and also it can use a well-known binder as a binder of a mixture -- the above-mentioned positive electrode -- a well-known additive etc. can be added to a mixture

[0045] Next, a positive-electrode sheet is cut down to band-like. And lead wire is welded to the agensis portion of a positive-active-material layer, and it considers as the positive-electrode terminal 7.

Aluminum, titanium, or these alloys are mentioned as an example of the material used for the positive-electrode terminal 7. Thus, the band-like positive electrode 2 is obtained.

[0046] moreover, the negative electrode in which a negative electrode 3 contains a negative-electrode active material and a binder -- in a mixture, by [used as a negative-electrode charge collector] applying and drying uniformly, for example on metallic foils, such as copper foil, a negative-electrode active material layer is formed and a negative-electrode sheet is produced here -- this negative electrode -- the scale-like graphite which is a negative-electrode active material at a mixture, and the scale-like graphite concerned -- in addition, the negative-electrode active material which consists of at least one or more kinds of carbon materials among nodular-graphite, massive graphite, fibrous graphite, and difficulty graphitized carbon or carbon black -- a mixture is used moreover, the above-mentioned negative electrode -- and also it can use a well-known binder as a binder of a mixture -- the above-mentioned

negative electrode -- a well-known additive etc. can be added to a mixture

[0047] Next, a negative-electrode sheet is cut down to band-like. And lead wire is welded to the agenesis portion of the negative-electrode active material layer of a negative-electrode charge collector, and it considers as the negative-electrode terminal 8. Copper, nickel, or these alloys are mentioned as an example of the material used for the negative-electrode terminal 8. Thus, the band-like negative electrode 3 is obtained.

[0048] Next, the gel electrolyte layer 4 is formed on a positive-active-material layer and a negative-electrode active material layer. In order to form the gel electrolyte layer 4, first, an electrolyte salt is dissolved in a non-aqueous solvent, and nonaqueous electrolyte is produced. And a matrix polymer is added to this nonaqueous electrolyte, it stirs well, a matrix polymer is dissolved, and a sol-like electrolytic solution is obtained.

[0049] Next, the specified quantity application of this electrolytic solution is carried out on a positive-active-material layer and a negative-electrode active material. Then, by cooling at a room temperature, a matrix polymer gels and the gel electrolyte layer 4 is formed on a positive-active-material layer and a negative-electrode active material.

[0050] And the band-like positive electrode 2 and band-like negative electrode 3 which were produced as mentioned above are made to rival through the gel electrolyte layer 4, are pressed, and let them be an electrode layered product. Furthermore, this electrode layered product is wound around a longitudinal direction, and it considers as the electrode winding object 5.

[0051] While inserting this electrode winding object 5 into the last with the sheathing film 6 which consists of an insulating material, and obturating the periphery marginal part of the sheathing film 6 at it and putting the positive-electrode terminal 7 and the negative-electrode terminal 8 between it at the obturation section of the sheathing film 6, the electrode winding object 5 is sealed in the sheathing film 6. Furthermore, it heat-treats to the electrode winding object 5 in the state where it packed with the sheathing film 6. The gel electrolyte cell 1 is completed as mentioned above.

[0052] In addition, although the case where carried out the laminating of the band-like positive electrode 2 and the band-like negative electrode 3, and wound around the longitudinal direction further and it considered as the electrode winding object 6 was mentioned as the example and the gestalt of operation mentioned above explained it, this invention is not limited to this, and when the laminating of the rectangle-like positive electrode 2 and the rectangle-like negative electrode 3 was carried out and being considered as the electrode layered product, or when an electrode layered product is folded up by turns, it can be applied.

[0053] Moreover, although the gel electrolyte cell 1 which used the gel electrolyte was mentioned as the example and the gestalt of operation mentioned above explained it as a nonaqueous electrolyte cell, this invention is not limited to this and can be applied also about the nonaqueous electrolyte cell using nonaqueous electrolyte, and the solid electrolyte cell using the solid electrolyte which does not contain a swelling solvent.

[0054] Furthermore, the nonaqueous electrolyte cell concerning this invention is not limited especially about the configuration, and can make a sheet type, cylindrical, a square shape, a coin type, etc. a thin shape and the various sizes of large-sized **. Moreover, this invention is [primary cell] applicable also about a rechargeable battery.

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EXAMPLE

[Example] Next, it is a book.

[0056] <Example 1> The negative electrode was produced as follows first.

[0057] the negative-electrode active material which serves as [nodular graphite] 99 weight sections from the powder which mixed 1 weight section in the ground scale-like graphite which is a negative-electrode active material -- a mixture -- as 90 weight sections and a binder -- poly (vinylidene fluoride-co-hexafluoropropylene) -- 10 weight sections -- mixing -- a negative electrode -- prepared the mixture, the N-methyl-2-pyrrolidone was made to distribute this further, and it considered as the shape of a slurry And this slurry was uniformly applied to both sides of band-like copper foil with a thickness of 20 micrometers which is a negative-electrode charge collector, compression molding was carried out with the roll-press machine after dryness, and the negative electrode was produced. In addition, the lead wire made from nickel was welded to the agenesis portion of the negative-electrode active material layer of a negative-electrode charge collector, and it considered as the negative-electrode terminal.

[0058] Moreover, the positive electrode was produced as follows.

[0059] First, a lithium carbonate and cobalt carbonate were mixed at a rate of 0.5:1 by the mole ratio, it calcinated at 900 degrees C among air for 5 hours, and LiCoO₂ used as a positive active material was obtained.

[0060] next, obtained LiCoO₂ -- as 91 weight sections and an electric conduction agent -- a graphite -- as 6 weight sections and a binder -- poly (vinylidene fluoride-co-hexafluoropropylene) -- 10 weight sections -- mixing -- a positive electrode -- prepared the mixture, the N-methyl-2-pyrrolidone was made to distribute this further, and it considered as the shape of a slurry And this slurry was uniformly applied to both sides of a band-like aluminum foil with a thickness of 20 micrometers which is a positive-electrode charge collector, compression molding was carried out with the roll-press machine after dryness, and the positive electrode was produced. In addition, the lead wire made from aluminum was welded to the agenesis portion of the positive-active-material layer of a positive-electrode charge collector, and it considered as the positive-electrode terminal.

[0061] Next, the gel electrolyte layer was obtained as follows.

[0062] First, propylene carbonate was mixed for ethylene carbonate with the 42.5 weight sections, 15 weight sections were mixed with the 42.5 weight sections for LiPF₆, and the plasticizer was prepared. In 30 weight sections of this plasticizer, 60 weight sections were mixed [poly (vinylidene fluoride-co-hexafluoropropylene)] with 10 weight sections for dimethyl carbonate, and the electrolytic solution was prepared in them.

[0063] On the positive-active-material layer and the negative-electrode active material layer, this electrolytic solution is applied uniformly, and was infiltrated, it was left in ordinary temperature for 8 hours, dimethyl carbonate was evaporated and removed, and the gel electrolyte layer was obtained.

[0064] And the 5cmx4cmx0.4cm electrode winding object was acquired by making the side in which the gel electrolyte layer was formed in the positive electrode produced as mentioned above and the negative electrode counter, and winding around lamination and a longitudinal direction.

[0065] The gel electrolyte cell was obtained by sealing this electrode winding object in the laminate film

which consists of a three-tiered structure of polypropylene / aluminum / nylon. In addition, the positive-electrode terminal and the negative-electrode terminal were put between the obturation section of a sheathing film at this time.

[0066] <an example 2> -- a negative-electrode active material -- except 95:5 having carried out comparatively the ratio of the scale-like graphite and nodular graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0067] <an example 3> -- a negative-electrode active material -- except 80:20 having carried out comparatively the ratio of the scale-like graphite and nodular graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0068] <an example 4> -- a negative-electrode active material -- except 70:30 having carried out comparatively the ratio of the scale-like graphite and nodular graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0069] <an example 5> -- a negative-electrode active material -- except 60:40 having carried out comparatively the ratio of the scale-like graphite and nodular graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0070] <an example 6> -- a negative-electrode active material -- except 50:50 having carried out comparatively the ratio of the scale-like graphite and nodular graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0071] <an example 7> -- a nodular graphite -- replacing with -- a massive graphite -- using -- a negative-electrode active material -- except 80:20 having carried out comparatively the ratio of the scale-like graphite and massive graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0072] <an example 8> -- a nodular graphite -- replacing with -- a massive graphite -- using -- a negative-electrode active material -- except 60:40 having carried out comparatively the ratio of the scale-like graphite and massive graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0073] <an example 9> -- a nodular graphite -- replacing with -- a fibrous graphite -- using -- a negative-electrode active material -- except 80:20 having carried out comparatively the ratio of the scale-like graphite and fibrous graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0074] <an example 10> -- a nodular graphite -- replacing with -- difficulty graphitized carbon -- using -- a negative-electrode active material -- except 80:20 having carried out comparatively the ratio of the scale-like graphite and difficulty graphitized carbon which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0075] <an example 11> -- a nodular graphite -- replacing with -- carbon black -- using -- a negative-electrode active material -- except 80:20 having carried out comparatively the ratio of the scale-like graphite and carbon black which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0076] <an example 12> -- the negative-electrode active material with which it comes to mix a scale-like graphite, a nodular graphite, and carbon black by the ratio of 80:15:5 -- except having used the mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0077] <an example 13> -- the negative-electrode active material with which it comes to mix a scale-like graphite, a nodular graphite, and a fibrous graphite by the ratio of 80:15:5 -- except having used the mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0078] <Example 1 of comparison> Except having used only the scale-like graphite as a negative-electrode active material, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode.

[0079] <the example 2 of comparison> -- a negative-electrode active material -- except 99.5:0.5 having carried out comparatively the ratio of the scale-like graphite and nodular graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0080] <the example 3 of comparison> -- a negative-electrode active material -- except 30:70 having carried out comparatively the ratio of the scale-like graphite and nodular graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0081] <Example 4 of comparison> Except having used only the nodular graphite as a negative-electrode active material, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode.

[0082] <the example 5 of comparison> -- a nodular graphite -- replacing with -- a massive graphite -- using -- a negative-electrode active material -- except 40:60 having carried out comparatively the ratio of the scale-like graphite and massive graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0083] <the example 6 of comparison> -- a nodular graphite -- replacing with -- a fibrous graphite -- using -- a negative-electrode active material -- except 40:60 having carried out comparatively the ratio of the scale-like graphite and fibrous graphite which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0084] <the example 7 of comparison> -- a nodular graphite -- replacing with -- difficulty graphitized carbon -- using -- a negative-electrode active material -- except 40:60 having carried out comparatively the ratio of the scale-like graphite and difficulty graphitized carbon which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0085] <the example 8 of comparison> -- a nodular graphite -- replacing with -- carbon black -- using -- a negative-electrode active material -- except 40:60 having carried out comparatively the ratio of the scale-like graphite and carbon black which constitute a mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0086] <the example 9 of comparison> -- the negative-electrode active material with which it comes to mix a scale-like graphite, a nodular graphite, and carbon black by the ratio of 40:40:20 -- except having used the mixture, the negative electrode was produced like the example 1 and the gel electrolyte cell was produced using this negative electrode

[0087] And about the gel electrolyte cell produced as mentioned above, the peel strength between negative-electrode charge collector-negative-electrode active material layers and the service capacity of a negative-electrode active material were measured, and the characterization examination of the load characteristic about the produced gel electrolyte cell and a cycle property was performed further.

[0088] The peel strength between negative-electrode charge collector-negative-electrode active material layers was measured by the so-called T character friction test.

[0089] As shown in drawing 4, the T character friction test stuck the adhesive tape 10 on the negative-electrode active material layer 3a front face of the negative electrode 3 with a width of face [of 30mm], and a length of 200mm, stuck this negative-electrode charge collector 3b side on the stainless steel board 11 further, and fixed A portion in drawing 4. This part was removed and it removed 10cm by pulling the removed edge to the stainless steel board 11 in the horizontal direction of drawing 4 Nakaya mark B, i.e., the direction. The average of the force required at this time was made into peel strength.

[0090] the negative-electrode active material same about the service capacity of a negative-electrode active material -- the coin type cell 20 as shown in drawing 5 using a mixture was produced, and it evaluated using this coin type cell 20

[0091] the negative electrode first obtained like an above-mentioned method as the creation method of

the coin type cell 20 -- the mixture was applied on the nickel mesh (20 micrometers of diameters of nickel fiber) used as a charge collector, it dried and the negative-electrode active material layer was formed. And the nickel mesh in which the negative-electrode active material layer was formed was used as the pellet-like negative electrode 21 by piercing to disc-like [with a diameter of 15.5mm].

[0092] Moreover, it considered as the positive electrode 22 by piercing a lithium metallic foil to a negative electrode and abbreviation isomorphism.

[0093] Moreover, nonaqueous electrolyte was prepared by dissolving LiPF₆ by the concentration of 1 mol/l into the amount mixed solvent of isochores of ethylene carbonate and propylene carbonate.

[0094] The negative electrode 21 obtained as mentioned above was held in the negative-electrode can 23, the positive electrode 22 was held in the positive-electrode can 24, and the separator 25 which consists of a porous membrane made from polypropylene between a positive electrode 22 and a negative electrode 21 was allotted. the inside of the positive-electrode can 24 and the negative-electrode can 23 -- nonaqueous electrolyte -- pouring in -- the positive-electrode can 24 and the negative-electrode can 23 -- an insulating gasket 26 -- minding -- the coin type cell 20 whose thickness a diameter is 20mm and is 2.5mm was produced by fixing in total

[0095] And about the obtained coin type cell 20, 10 hour-rate charge of geometric capacity was performed to minimum 0V by constant-voltage constant-current charge, and, next, 10 hour-rate constant-current discharge was performed among final-voltage 1.5V. Service capacity at this time was made into the service capacity of a negative-electrode active material.

[0096] As a load characteristic, about the gel electrolyte cell, 1 / 3 hour-rate electric discharge of geometric capacity (3C) were performed first, and it evaluated as follows. First, to each cell, 23 degrees C and constant-current constant-potential charge were performed to 4.2V for 10 hours, next, constant-current discharge of 3C was performed among final-voltage 3.2V, and service capacity was determined. And the output in each hour-rate electric discharge was computed as 100 molar fractions to 1/5C from the average voltage called for from now on. Moreover, the volume energy density of the cell to the service capacity at this time was computed.

[0097] As a cycle property, to each cell, constant-current constant-potential charge was performed to upper limit 4.2V at 23 degrees C, next constant-current discharge of 2 hour-rate electric discharge (1/2C) of geometric capacity was performed among final-voltage 3.2V. It is 500 cycle ***** , using this as 1 cycle. And the output in hour-rate electric discharge was computed from the average voltage called for from now on as 100 molar fractions to 1/5C in early stages of a cycle (the 1st cycle eye).

[0098] Each cell characterization result about the cell of an example 1 - an example 13, the example 1 of comparison - the example 9 of comparison is shown in Table 1.

[0099]

[Table 1]

	添加炭素材料 種類	炭素材料添 量(Wt%)	負極厚み (μm)	負極剝離 強度(g/mm)	放電容量 (mAh/g)	負荷特性 (%)	3C放電のエネルギー 密度(WA/l)	サイクル 特性(%)
実施例1	球状黒鉛	1	100	9.4	358	70	321	66
実施例2	球状黒鉛	5	103	15.6	358	76	338	78
実施例3	球状黒鉛	20	106	20.3	352	82	360	83
実施例4	球状黒鉛	30	109	24.8	350	81	364	83
実施例5	球状黒鉛	40	115	23.6	348	83	350	84
実施例6	球状黒鉛	50	121	23.3	343	84	326	87
実施例7	塊状黒鉛	20	105	16.2	352	80	338	81
実施例8	塊状黒鉛	40	106	18.2	352	78	342	80
実施例9	繊維状黒鉛	20	106	14.6	370	72	332	65
実施例10	難黒鉛化炭素	20	126	15.3	378	76	301	70
実施例11	カーボンブラック	20	106	11.2	348	74	322	50
実施例12	球状黒鉛+カーボンブラック	15+5	106	19.4	345	76	327	77
実施例13	球状黒鉛+繊維状黒鉛	15+5	107	21.8	355	78	342	79
比較例1	—	0	100	3.3	360	34	168	33
比較例2	球状黒鉛	0.5	100	3.2	360	35	163	32
比較例3	球状黒鉛	70	125	24.2	338	86	320.2	88
比較例4	球状黒鉛	100	140	24.3	330	89	295	90
比較例5	塊状黒鉛	60	123	16.9	344	81	312	81
比較例6	繊維状黒鉛	60	124	17.8	350	78	314	79
比較例7	難黒鉛化炭素	60	126	15.3	378	76	301	70
比較例8	カーボンブラック	60	130	10.7	327	74	264	49
比較例9	球状黒鉛+カーボンブラック	40+20	131	22.1	335	76	271	76

[0100] First, when it sees about the peel strength between negative-electrode charge collector-negative-electrode active material layers, in the example 2 of comparison whose example 1 of comparison and addition which did not add a carbon material are 0.5 % of the weight, peel strength is extremely low and

it turns out that a negative-electrode active material layer tends to exfoliate from a negative-electrode charge collector. Although peel strength also increases with the increase in the rate of the added carbon material, even if it will be saturated if the rate of a carbon material becomes about 20% of the weight and the addition rate of a carbon material increases after it, most improvement in peel strength is not found.

[0101] Moreover, the cycle property of a cell is also known by that the good value is acquired, so that the peel strength between negative-electrode charge collector-negative-electrode active material layers becomes large.

[0102] On the other hand, the rate of a negative-electrode active material will fall and service capacity will fall as the addition rate of a carbon material increases. Moreover, although the improvement effect is notably seen to about 5 % of the weight, if the addition rate of a carbon material becomes more than it also about a load characteristic, the property of an addition carbon material will come to appear strongly, and the improvement effect of a load characteristic will no longer be seen so much.

[0103] Moreover, the thickness of a negative electrode is thick and a bird clapper is known as the addition of a carbon material increases, when it is going to make equal service capacity per unit area of a cell. This means reducing the volume energy density of a cell by adding a carbon material. About the volume energy density at the time of 3C electric discharge, when the additions of a carbon material are 5 % of the weight or more and 30 % of the weight or less, it turns out that the good value is acquired.

[0104] When the addition of the carbon material added from the above result to the scale-like graphite which is a negative-electrode active material is made into 1 % of the weight or more and 50% of the weight of the range, it turns out that the desirable result is obtained. Also in it, when the addition of a carbon material is made into 5 % of the weight or more and 30% of the weight or less of the range, it turns out that the desirable result is obtained especially.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the perspective diagram showing the example of 1 composition of the gel electrolyte cell concerning the gestalt of this operation.

[Drawing 2] It is a cross section in X1-X2 line among drawing 1.

[Drawing 3] A positive electrode and a negative electrode are the perspective diagrams showing the state where it is considered as the electrode winding object.

[Drawing 4] It is the cross section showing the method of the peel strength examination in an example typically.

[Drawing 5] It is the cross section showing the example of composition of the coin type cell used by evaluation of negative-electrode service capacity.

[Description of Notations]

1 Gel Electrolyte Cell 2 Positive Electrode 3 Negative Electrode 4 Gel Electrolyte Layer, 5 Electrode Winding Object 6 Sheathing Film 7 Positive-Electrode Terminal 8 Negative-Electrode Terminal

[Translation done.]

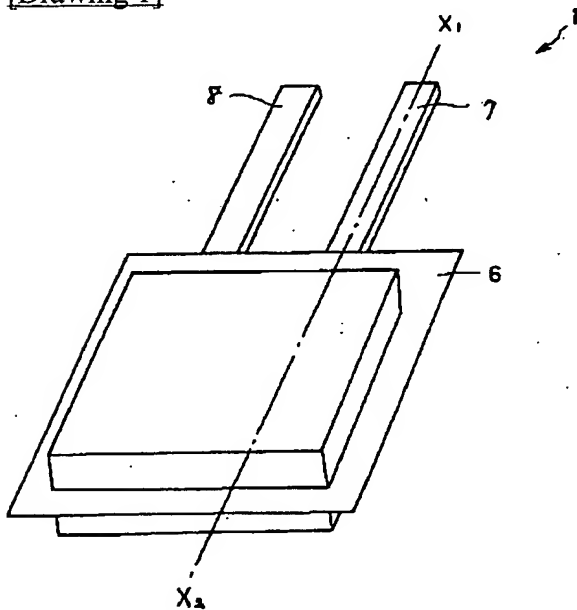
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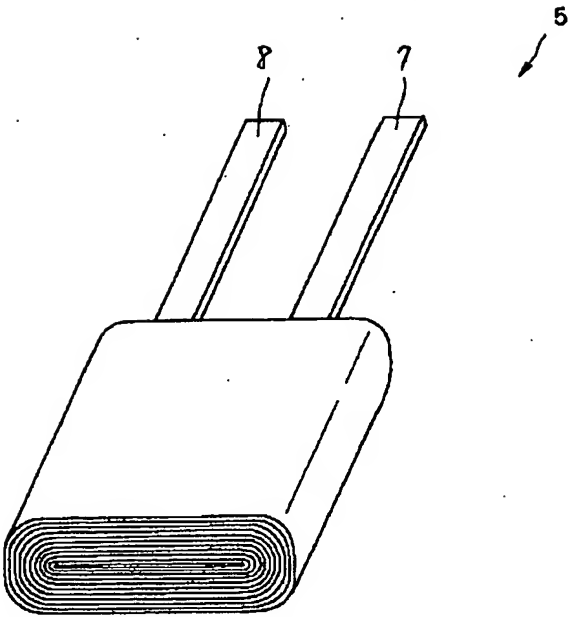
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DRAWINGS

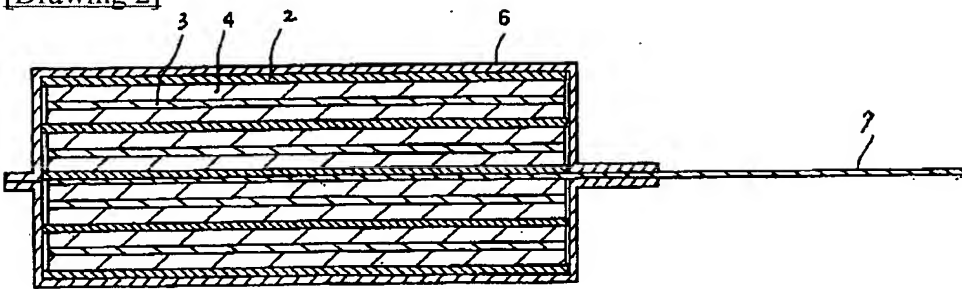
[Drawing 1]



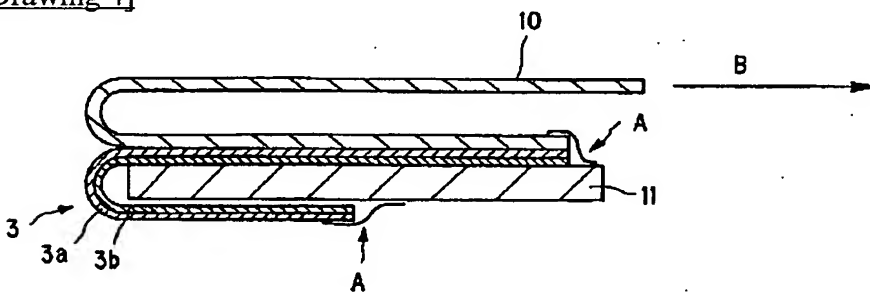
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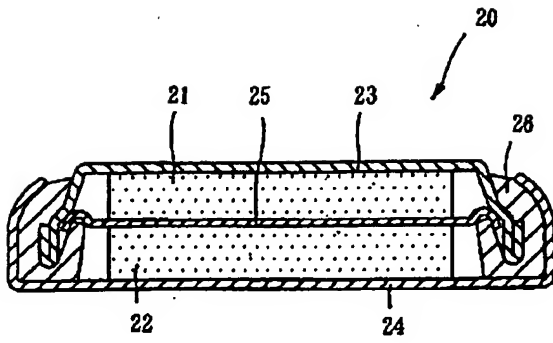
[Drawing 2]



[Drawing 4]



[Drawing 5]



[Translation done.]